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(54) Title: THERMOPLASTIC RUBBER COMPOSITION

(57) Abstract

A rubber matrix including a) 10–90 % (v/v) of natural rubber, b) one or more first compatabilisers selected from a group of polymers containing either i) a nitrile group, ii) a halogen, iii) an acetate group, iv) an epoxide, v) a styrene, or vi) an acrylate and c) one or more second compatabilisers which are interfacial copromoters selected from a group comprising either i) polyvinyl acetate, ii) ethylene vinyl acetate, iii) polyacrylonitrile or high nitrile resin, iv) acrylamide or polyacrylamide, v) a phenolic resin, vi) an acrylate polymer, vii) a halogenated polymer, viii) maleic anhydride or polymaleic anhydride, or ix) a bismaleimide. The rubber matrix may be mixed with one or more thermoplastics selected from a group comprising either i) polyurethanes, ii) polyesters, iii) polyamides, iv) acrylates, v) acrylonitrile butadiene styrene, vi) polyolefins, or vii) cellulose esters to form a rubber thermoplastics composite.

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THERMOPLASTIC RUBBER COMPOSITION

The present invention is directed to a rubber matrix composition including natural rubber with the capacity to form a thermoplastic composite with a range of thermoplastics.

BACKGROUND OF THE INVENTION

Natural rubber has been used for a variety of purposes over time however, there are some properties which make rubber more difficult to use in industrial processes and/or make it unsuitable for certain applications. These properties include having a high molecular weight, high viscosity, often being contaminated with naturally occurring proteins and often having a high dirt content. Additionally rubber as it is generally used is cross linked by vulcanisation. These cross-links are difficult to reverse and as a consequence recycling of used rubber products is difficult to satisfactorily achieve.

Natural rubber also has some very desirable properties compared to plastics and some other rubbers which properties include, toughness, dynamic sealing properties, resilience, flex fatigue life, low compression and tension set, and low flex modulus and creep. There has been a desire therefore to blend natural rubber and certain thermoplastics to make a composite having the desirable properties of rubber but processable and reprocessable as thermoplastics.

A considerable amount of work has been conducted into blending natural rubber with a variety of plastics to enhance the properties of natural rubber. The great difficulty witn this blending is that natural rubbers are substantially non-polar and cannot give an effective blend with some plastics. Additionally the high molecular weight and the variation of molecular weight of natural rubber make uniform blending difficult. The greatest success has been in the blending of natural rubbers with a limited range of plastics including polypropylene, polyethylene, polystyrene, methyl-methacrylate, ethyl vinyl acetate and polyvinyl acetate. However limited success has been had blending with increasingly popular plastics including polyamides, polyurethanes, polyesters and acrylonitrile butadiene styrene (ABS). Similar blends have been attempted with synthetic rubbers such as butadiene rubbers and isoprene rubbers.

Blends between thermoplastics and natural or synthetic rubbers have been facilitated in the past in a number of ways by introducing polar compounds into the natural or

synthetic rubber and one such approach has been to introduce acrylonitrile into natural rubbers and synthetic rubbers to facilitate such a blending.

There is, to the knowledge of the inventor, no available system that provides for the capacity to reliably blend natural rubber with a large range of thermoplastics.

OBJECT OF THE INVENTION

It is an object of the present invention to provide a rubber matrix that permits the formation of composites of any one or more of a wide range of thermoplastics with natural rubber.

SUMMARY OF THE INVENTION

In one broad form of a first aspect the invention could be said to reside in a rubber matrix including

a) natural rubber 10-90%(v/v)

b) one or more first compatabilisers selected from a group of polymers containing either

i) a nitrile group,
ii) a halogen,
iii) an acetate group,
iv) an epoxide,
v) a styrene, or
vi) an acrylate

c) one or more second compatabilisers which are interfacial copromoters selected from a group comprising either

i) polyvinyl acetate,
ii) ethylene vinyl acetate,
iii) polyacrylonitrile or high nitrile resin,
iv) acrylamide or polyacrylamide,
v) a phenolic resin,
vi) an acrylate polymer,
vii) a halogenated polymer,
viii) maleic anhydride or polymaleic anhydride, or

ix) a bismaleimide.

The rubber matrix may be mixed with a range of thermoplastics to form thermoplastic rubber composites. The thermoplastic may be selected from one or more of the group including, but not limited to polyolefins, polyamides, polyesters, polyurethanes, polystyrene, acrylonitrile butadiene styrene, all of which will be described in detail later.

Preferably the first and second compatabilisers are different.

An advantage of thermoplastics is that they are recyclable and/or reprocessable and can be re-moulded. Preferably the thermoplastic rubber composite formed by mixing the rubber matrix of the present invention with a thermoplastic can similarly be recycled, reprocessed, and/or re-moulded.

The natural rubber is preferably selected from the grades known as deproteinated natural rubber (DP-NR), oil extended natural rubber (OE-NR), peptised natural rubber, superior processing rubber (SP or PA), standard Malaysian rubber (SMR) constant viscosity (SMR-CV), low viscosity (SMR-LV), or general purpose (SMR-GP) grades or ISNR LCV grades. These grades tend to have a low protein and low dirt content. Most preferably SMR or ISNR LCV grades are used.

The content of natural rubber in the rubber matrix may be between 10 phr and 90 phr (parts per hundred rubber). Preferably the rubber matrix has between 35 phr to 40 phr natural rubber for the desirable elastoplastic properties of the natural rubber to be transferred to a final product. If less than 10 phr of natural rubber is used in the rubber matrix the desirable properties of natural rubber tend not to be inherent in the final product.

It may be desired to replace up to 50% of the total quantity of rubbers with reclaimed rubbers from a variety of sources including but not limited to car tyres. It may also be desired to replace at least a part of the plastic component of the thermoplastic rubber composite with graded recycled plastics.

The molecular weight of natural rubber is high and it is a highly viscous and resilient rubber. The normal process involved with blending natural rubber with plastics is to

break down the molecular weight of natural rubber so as to match it with the size of the plastic in order to get effective blending. However the present invention is believed to work at least in part by preventing the natural rubber, which is a highly resilient material and normally regains its molecular weight, from creating a discontinuous phase between the blending plastic and that of the natural rubber. In the present case it is thought that this problem is overcome by the addition of a polar rubber which also has a lower molecular weight and creates a better base and a better match between the rubber and the plastic phases. The lower molecular weight is thought to reduce and stabilise the viscocity of the rubber phase, which in turn increases the flow characteristics. The polar compounds also are also thought to increase the attractive forces between the plastics and rubber phases. In addition the polar groups increase the resistance of natural rubber to oils and polar petrochemical based fluids.

Depending on the thermoplastic used and the ratios of the components of a final composition, a range of thermoplastic compositions each having different properties may be formed. The properties may be tailored to suit a particular application. Thus a range of soft composites may be formed by compounding the rubber matrix with polyolefins, polyvinyls or polyurethanes for example. In contrast intermediate composites may be produced by compounding the rubber matrix with polyurethanes, polyamides, polyvinyls or polyesters for example. Rigid composites may be produced by compounding the rubber matrix with polyolefins, polyurethanes or polyamides for example.

When the rubber matrix is to be used for soft composites, such as with polyolefins, the natural rubber content in the rubber matrix is preferably about 20-70% and most preferably about 40%, with the rubber matrix and plastics preferably being blended in relative proportions of 5-70 parts to 95-30 parts to a total of 100 parts respectively. Generally, if the rubber matrix comprises more than 75 parts per hundred of the total composite the flow of the composite will be restricted and a continuous phase may not form in the composite. The plastics in such soft composites might be selected from the group comprising polypropylene, polyethylene, polyvinyl acetate, ethylene vinyl acetate, ethylene propylene plastic (Engage; DuPont), polyurethanes or polyvinyl chloride.

The first compatabiliser is selected to have good natural rubber blending properties, and also to present a polar group for attraction by the second compatabiliser. The first

compatabiliser is also thought to stabilise the viscosity of natural rubber. At least some of the properties of the first compatabiliser will be transferred to the final composition, the degree of which will be determined in part by the amount of first compatabiliser in the final composition.

A nitrile based first compatabiliser may be selected from: an acrylonitrile diene rubber such as nitrile isoprene rubber or nitrile butadiene rubber; nitrile natural rubber; polyacrylonitrile; high nitrile polymer. The amount of nitrile based compatabiliser added to the rubber matrix will be determined by the desired properties of the final composition, but is preferably greater than 10% of the rubber matrix.

The nitrile butadiene, nitrile isoprene and nitrile natural rubber preferably has an acrylonitrile content of over 20%. The nitrile content will improve the oil and fuel resistance of the rubber. Further, the elastic behaviour of the nitrile rubbers becomes poorer as the nitrile content increases however at the same time the polymer becomes more thermoplastic which is advantageous regarding the processability of the compounds. The compatibility with polar plasticisers or polar plastics improves with increasing nitrile content.

High nitrile polymers having a nitrile content of more than about 50% may also be used. For example Barex 210 (B-210) (BP America Inc) is a commercially available acrylonitrile-methyl acrylate-butadiene (70:21:9 parts by weight) polymer. These polymers have excellent barrier properties and are useful in packaging solids, liquids and gases of various types.

A halogenated first compatabiliser may be a halogenated polymer selected from: chlorinated rubber; polyvinyl chloride; polychloroprene (Neoprene; DuPont); vinyl diene fluoride. Chlorinated polyethylene or chlorosulphonated polyethylene (e.g. Hypalon; DuPont) are slow curing polymers that are also suitable halogenated first compatabilisers when used in conjunction with polychloroprene. Alternatively the rubber matrix may be halogenated *in situ* by the addition of a halogen source such as N-bromosuccinimide. A further alternative is to introduce halogen into the composition by the inclusion of chlorinated paraffin oil. Preferably the halogenated compatabiliser is used in conjunction with a nitrile compatabiliser.

To retain at least some of the desirable properties of the halogenated compatabiliser preferably the halogen containing polymer comprises greater than 15% of the rubber matrix. A rubber matrix containing a halogen based first compatabiliser will be particularly suited to blending with polyvinyl chloride, polyamides, polyurethanes and/or polyesters.

An epoxide based first compatabiliser may be an epoxidised natural rubber preferably formed by the reaction of natural rubber with hydrogen peroxide/formic acid/acetic acid. Preferably the epoxide based compatabiliser has an epoxide content of 20 to 50% to give a rubber matrix having an epoxide content of 10 to 25%.

An acetate containing first compatabiliser may be selected from: polyvinyl acetate; ethylene-vinyl acetate containing a relatively high vinyl acetate content; a vinyl acetate rubber. Preferably the acetate polymer comprises 20 to 50% of the rubber matrix and more preferably comprises 30%, and the rubber matrix has a vinyl acetate content of greater than 20%.

An acrylate based first compatabiliser may be selected from: an acrylic rubber such as Vamac (Dupont), or one formed from the following monomers: ethyl acrylate; methyl acrylate; methyl methacrylate. Preferably the acrylate compatablilser is used in conjunction with a nitrile compatabiliser in about equal ratios. The combination of acrylic and nitrile first compatabilisers is particularly suited to blending with polyamides or acrylates.

A styrene based first compatabiliser may be selected from: styrene natural rubber; styrene butadiene rubber; styrene isoprene styrene block coploymer (SIS) (e.g. Kraton; Shell); styrene ethyl butylene styrene block copolymer (SEBS). A rubber matrix containing a styrene based first compatabiliser may be particularly suited to blending with a styrene thermoplastic such as polystyrene or an acrylonitrile butadiene styrene (ABS).

A combination of more than one of the first compatabilisers may be used in the rubber matrix so as to impart at least some of the characteristics of each of the compatabilisers onto the rubber matrix. For example nitrile rubbers may impart a degree of swell resistance to the rubber matrix such that a final composition may have increased resistance to oils, fuels and fats. Similarly halogenated rubbers, and in particular

chlorinated rubbers, are fire resistant and therefore incorporation of them into the rubber matrix will increase the fire resistance as well as the swell resistance of the final product. Thus, a preferred combination of first compatabilisers is a nitrile rubber and a chlorinated rubber which will tend to increase the resistance of a final composition to fire and to petrochemical based solvents and oils.

The second compatabiliser is chosen to provide a greater polarity or charge density within the rubber phase of a composite to facilitate blending with thermoplastics that do not readily blend with the first compatabiliser. The choice of second compatabiliser is not restricted to those compounds that can interact with the largely non-polar rubber and still present a polar group. They are selected so as to be able to interact with, for example the polar group presented by acrylonitrile, and then present a further polar group with greater polarity or charge density to thereby increase the range of plastics that can be mixed with the rubber matrix. It has been found that in many instances natural rubber is incompatible with, for example, a nitrile rubber-polar thermoplastic blend. However upon addition of a second compatabiliser it is possible to incorporate natural rubber and achieve a continuous phase thermoplastic elastomer composition.

When polyvinyl acetate, ethylvinyl acetate, acrylamide or polyacrylamide, polyacrylonitrile or high nitrile resin, an acrylate polymer, a halogenated polymer, maleic anhydride or polymaleic anhydride, or a bismaleimide is used as a second compatabiliser it is possible to achieve good compounding with the group including but not limited to polyamides, polyurethanes, polyesters, polystyrene including high impact polystyrene, acrylonitrile butadiene styrene, as well as the more readily blended plastics such as the polyolefins.

Aspects of the present invention involve the formation of two phases, a rubber matrix as a rubber phase and a thermoplastics component in a plastics phase, and the invention thus involves a first mixing of components to form the rubber matrix. Combining the rubber matrix with the plastics phase involves a second mixing of the rubber matrix (rubber phase) with the plastics phase. The rubber matrix is substantially a rubber phase and acts as an intermediate. The rubber matrix can be tailored to be combined with any one of a number of different thermoplastics. Preferably the ratio of rubber phase to plastic phase is between 5:95 and 90:10, however compositions having greater than about 75% rubber phase tend to have a high viscosity and do not flow easily and therefore may be of limited use. To achieve thermoplasticity in the final composition

the composition is required to have a continuous plastic phase and therefore the plastic phase should comprise at least 10% of the final composition. These portions are necessary to provide sufficient rubber to give elastomeric compositions and sufficient plastic to provide thermoplasticity. The ratio of rubber to plastic can be altered within these limits to form a composition having the desired characteristics.

The rubber phase (or rubber matrix) is formed first and includes the steps of mixing components of the rubber phase including a) the natural rubber; b) a first compatabiliser and, c) a second compatabiliser and d) any further additives that might be required. The rubber phase is formed in a cold mixing process. Such a cold mixing process will typically be performed at a temperature of less than about 120°C. The cold mixing is thought to reduce the particle size of the natural rubber to below about 50μ thus forming an intimate mixture of natural rubber particles dispersed in the rubber matrix. After mixing or masticating the rubber phase is normally viscosity stabilised once it is formed and may be left to mature before inclusion in a second mixing as described below.

The first compatabiliser, apart from providing polarity to the rubber matrix, in particular is thought to stabilise the viscosity of the natural rubber in the matrix and prevent the normal tendency of the rubber to regain its molecular weight thus creating a discontinuity between the plastics phase and the natural rubber. The second compatabiliser is then thought to provide further polarity to the matrix so that a range of polar thermoplastics are compatible with the matrix.

A second mixing may be carried out using any of the known methods such as melt mixing or dynamic vulcanisation. Dynamic vulcanisation is preferred and may be carried out using conventional masticating equipment, for example a Banbury mixer, Brabender mixer, mixing extruder or a twin screw extruder. The conditions of high shear provided under dynamic vulcanisation conditions provides for dispersal of the rubber phase and plastics phase. Thus the mixture of rubber and plastics phases are treated under temperature and time conditions that result in the desired level of crosslinking between the rubber and the plastic. The thermoplastic composition is formed by mixing the plastics phase and the rubber phase and masticating the mix at a temperature sufficient to at least soften the plastic, but more preferably a temperature above the melting point of the plastic. So as to minimise thermal degradation of the rubber matrix it is preferable that the plastic melts at less than 205°C. Representative temperatures may include but are not limited to: for polypropylene 170°C; polyethylene

130-150°C; polyamide 180-200°C; thermoplastic polyurethane 180-200°C; polyester 200°C. It is preferable that the melt temperature of the plastic is less than 205°C because the natural rubber will tend to degrade above this temperature. Heating and masticating at these temperatures is usually sufficient to allow cross link formation.

Compositions of the invention may also be prepared by methods other than dynamic vulcanisation. Thus a fully vulcanised rubber phase may be powdered and mixed with the plastics phase and provided that the rubber particles are small and there is sufficient match between the size of the rubber particles and the plastics, a composition having rubber particles well dispersed in the plastics phase can be formed.

The mixing of the rubber matrix with the plastics phase will require the addition of a curative agent to allow the formation of cross links within the rubber matrix. However it will be understood that when certain plastics such as ethylene vinyl acetate or polyethylene are used there may be some cross linking of the plastic with itself and/or with the rubber matrix. Any of the curative systems typically used in rubber vulcanisation can be used. Thus the curative system may be selected from the group comprising but not limited to: a dimethylol phenol system (e.g. SP1045; Schenctady); a bismaleimide system (HVA_2); a bismaleimide MBTS system; a bismaleimide peroxide system; an organic peroxide system; an accelerated sulphur system; a urethane system (e.g. Novar 924); a borane system; a radiation system. Preferably the curative agent is a cross linking agent such as a peroxide bismaleimide system. Alternatively, or in addition, the curative may include an interfacial promoter such as for example phenylene bismaleimide (HVA_2, Dupont), ethylene glycol dimethacrylate (Perkalink 401; Akzo Nobel), trimethylo propane trimethacrylate (Perkalink 400; Akzo Nobel), triallyl isocyanourate (Perkalink 300; Akzo Nobel) or triallyl cyanourate (Perkalink 301; Akzo Nobel). The interfacial promoter may also act as stabilisers in an overall peroxide/urethane cross linking system.

An advantage of a peroxide curative system may be the creation of cross links between the plastic and rubber phases when the peroxide is used in conjunction with SARET/HVA_2, and use of a peroxide curative system may lead to a composite having improved tensile strength and improved high temperature strength. However peroxide curative systems can not be used in direct contact with polypropylene due to the action of peroxide degrading the plastic, however they may be used in a rubber matrix which is subsequently mixed with polypropylene. Further, it may not be possible to use

peroxide curing systems with maleic anhydride in an open system due to potential for ignition in contact with air. Peroxide curative systems are preferably not used with chloroprene rubbers, in which case magnesium oxide or zinc oxide may be used as curatives preferably in conjunction with phenolic resins.

Any of the peroxide curative systems known in the art may be used in the present invention. The peroxide may be chosen from the group including, but not limited to, dicumyl peroxide, di-tert-butyl peroxide, di (2-tert-butyl peroxy isporopyl) benzene. The peroxides may be supported on an inert carrier. Peroxide curative systems are less commonly used when the total rubber content in the final composition is less than 15% unless HVA_2 or SARET are present. Typically when the total rubber content in the final composition is less than 15%, HVA_2 may provide sufficient cross linking however small amounts of peroxide may be used to assist in the cross linking. If HVA_2 or SARET are not present the peroxides are likely to degrade the polypropylene and thus the composition may lose the desirable properties.

A sulphur based curative system will not create cross links between the plastic and rubber phases and the resultant composition will have a lower compression set and better tensile properties than a composition having the rubber and plastics phases cross linked.

In compositions where the total rubber matrix is greater than 20% of the overall composition, the curative agents are preferably added to the rubber matrix while masticating, that is at the first mixing stage. In the case where the rubber matrix content is between 10% and 20% of the total composition the HVA_2 should be added to the plastic phase and the peroxide to the rubber phase. When there is less than 10% rubber matrix in the total composition peroxide should not be used and other curatives such as an accelerated sulphur system or a phenolic system may be used if required.

The properties of the thermoplastic rubber composition may be modified by the inclusion of additives which are conventional in the compounding of rubbers and/or thermoplastics. Additives that might be used could include heat stabilising chemicals, flame retarding chemicals, peptising agents, fillers, extenders, plasticisers, pigments, accelerators, stabilisers, antidegradants such as anti-oxidants and UV filters, processing aids and extender oils.

Where halogen containing radicals such as tin chloride or chlorinated paraffin oil are used in a composition, magnesium oxide or maleic acid may be added to the composition to act as scavengers and/or pH stabilisers.

Suitable UV filters may be selected from one or more of the group including, but not limited to, Tinuvan P (Ciba Geigy), titanium dioxide or carbon black. Tinuvan P is preferably added according to the manufacturers directions. Titanium dioxide or carbon black are preferably added at about 2.5 parts per hundred parts of the final composition.

Suitable plasticisers may be selected from one or more of the group including, but not limited to, aromatic, naphthenic and paraffinic extender oils, phthalate plasticisers, sulphonamide plasticisers, adipate plasticisers or phosphate plasticisers. Preferred plasticisers are dehydrated castor oil which may be added at 0.8 phr of rubber content, and cumarone and indene resins are ideally suited for the compositions of the present invention at levels up to 5 phr.

Processing aids may include internal lubricants to increase flow and enhance mixing particularly during the mastication stage. Suitable lubricants may include zinc or magnesium salts. Preferably the lubricant is zinc stearate which is added during mastication. The zinc stearate is readily added in the form of zinc oxide (e.g. from about 5 to about 15 phr) plus stearic acid (e.g. from about 1 to about 5 phr). The rest of the curing system is ordinarily kept apart from the elastomer until just prior to curing.

Reinforcing fillers may be selected from the group comprising, but not limited to, carbon black, clays, minerals such as talc and silica. Fillers tend to increase the tensile strength of the final composition. Fillers may be added up to levels of 30phr. Loadings beyond this level tend to impair the flow of the composite. Polypropylene homopolymer may also be added to balance mould shrinkage caused by the addition of fillers.

Heat stabilising additives may be selected from the group comprising, but not limited to, phenolic resins (e.g those available from Hylam Bakelite); Flectol H; chlorinated rubbers.

Suitable antioxidants may be selected from one or more of the group including, but not limited to, Wingstay L/100 (Goodyear); di-naphthyl-*p*-phenylene diamine (Santowhite

CI, Monsanto); styrenated phenol (Montaclere-SE, Monsanto); 2,5-di(tert-amyl) hydroquinone (Santovar-A, Monsanto); 4,4'-butylidenebis-(6-tert-butyl-m-cresol) (Santowhite, Monsanto); tributyl thiourea (Santowhite-TBTU, Monsanto); 6-tert-butyl-m-cresol/sulfur dichloride (Santowhite-MK, Monsanto); trinonyl phenylene phosphate (TNNP; Ciba Geigy). Preferably antioxidants are added at 1 to 2 % of the total composition.

Antidegradants that may be added could include ethylene propylene diene terpolymer (EPDM) rubbers. These can be added at 5% of the total composition to improve the weatherability of the composition. Levels over 5% may have an adverse impact on curing because EPDM are slow curing rubbers.

Peptising agents may be selected from any of those known in the art, such as Renacit 11 (Bayer). These agents are preferably added at about 0.07 % of the total composition.

In a second aspect the invention might also be said to reside in a natural rubber thermoplastics composite of a rubber matrix of the first aspect of the invention blended with any one or more of the thermoplastics selected from the group comprising polyolefins, polyurethanes, polyesters, polyamides, acrylates, acrylonitrile butadiene styrene (ABS).

Thus in one broad form of a second aspect the invention could be said to reside in a natural rubber thermoplastics composite including

a) natural rubber 10-90%(v/v)

b) one or more first compatabilisers selected from a group of polymers containing either
   - i) a nitrile group,
   - ii) a halogen,
   - iii) an acetate group,
   - iv) an epoxide,
   - v) a styrene, or
   - vi) an acrylate

c) one or more second compatabilisers which are interfacial copromoters selected from a group comprising either

i) polyvinyl acetate,
ii) ethylene vinyl acetate,
iii) polyacrylonitrile or high nitrile resin,
iv) acrylamide or polyacrylamide,
v) a phenolic resin,
vi) an acrylate polymer,
vii) a halogenated polymer,
viii) maleic anhydride or polymaleic anhydride, or
ix) a bismaleimide

d) one or more thermoplastics selected from a group comprising either

i) polyurethanes,
ii) polyesters,
iii) polyamides,
iv) acrylates,
v) acrylonitrile butadiene styrene,
vi) polyolefins, or
vii) cellulose esters.

Most preferably the thermoplastic is more polar than natural rubber, such thermoplastics including polyurethanes, polyesters, polyamides, acrylates, acrylonitrile butadiene styrene or celluloses. It will be appreciated that some slow curing rubbers such as butyl rubber may not be particularly suitable in the practice of this invention because of their undesirable curing properties. Further, when the thermoplastic is selected from the group of polyolefins and the first compatabiliser is selected from the group of halogenated polymers, then preferably the second compatabiliser is not a phenolic resin or a halogenated polymer.

Optionally, a least part of the thermoplastic used in the composite may be derived from recycled thermoplastics.

Suitable polyolefins may be selected from the group including but not limited to high density polyethylene (HDPE), linear low density polyethylene (LLDPE), polypropylene homo polymer (PPHP), polyproylene copolymer (PPCP), poly(ethylene-co-propylene)

(PEP). Polyolefins may be chosen for their high chemical resistance, electrical properties, high impact strength and low cost.

Suitable thermoplastic polyamides include those that are crystalline or resinous high molecular weight copolymers or terpolymers. Polyamides may be prepared by polymerisation of one or more lactams such as caprolactam, pyrrolidinone, lauryllactam, or by condensation of diamines with diacids. Suitable polyamides include polymeric amides having recurring amide groups as part of the polymer backbone and may be chosen form the list including but not limited to polycaprolactam (Nylon-6), polylauryllactam (Nylon-12), polyhexamethyleneadipamide (Nylon-6,6), polyhexamethyleneazelamide (Nylon-6,9), polyhexamethylenesebacamide (Nylon-6,10), polyhexamethyleneisophthalamide (Nylon-6,IP), the condensation product of 11-aminoundecanoic acid (Nylon-11) and the product of reaction between castor oil and sebasic acid. Suitable polyamides also include copolymers with other monomers. Polyamides may be chosen for their high impact strength, shock resistance, high tensile strength, ability to absorb moisture and/or their flame resistance.

Suitable polyurethanes may include but are not limited to thermoplastic polyurethane resins based on caprolactam, ethylene glycol or ethyl or propyl adipate reacted with isocyanates and having a Shore A hardness of 80 to 90. Polyurethanes may be chosen for their desirable properties that may include their toughness and abrasion resistance.

Many commercially available thermoplastic polyesters may be suitable and the polyesters may be prepared by condensation of one or more dicarboxylic acids, anhydrides or esters and one or more diol. Cellulosic polyesters are particularly suitable for the present invention and suitable cellulosics can include but are not limited to polymers of cellulose acetate, cellulose acetobutyrate or cellulose propionate. Suitable polyesters may also include polycarbonates.

Suitable acrylic thermoplastics may include polymethyl methacrylate and these may be added to improve heat stability and coulourability of a final composition. Further, acrylics tend to be highly crystalline and therefore they are preferable when a highly crystalline final composition is required.

The rubber thermoplastic compositions of the present invention may be divided into one of four classes depending upon the properties of the composition, namely rigid, toughened, semi-toughened or soft natural rubber thermoplastic compositions.

The rubber thermoplastic compositions of the present invention are intended for use as thermoplastic elastomers that are processable and can be fabricated into parts by conventional techniques used for thermoplastic materials. The mechanical properties of the compositions of the present invention may be determined using the standard test procedures used in the rubber and thermoplastics industries.

Thermoplastic rubber compositions of the present invention may be used for making articles used in the mechanical, automotive, construction, textile, sports goods, irrigation, cable, agriculture, footwear, pipe/hose and tyre and wheel industries. The articles may be made by extrusion, injection moulding or compression moulding.

In a third aspect the invention might also be said to reside in an article made from a thermoplastic composite of the present invention, which article may be formed by any suitable method used in the thermoplastics industries, which methods may include extrusion, injection moulding or compression moulding.

In a fourth aspect the invention might also be said to reside in a method of forming a natural rubber thermoplastics composite, including the steps of forming a rubber matrix of the first aspect of the invention, and combining the rubber matrix with a plastics phase under conditions of dynamic vulcanisation.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding, the invention will now be described with reference to a number of examples which are also represented in the Figures wherein,

Figure 1 shows weight loss versus temperature results of differential scanning calorimetry of a sample 'soft' grade sample of natural rubber/nitrile rubber/polyolefin,

Figure 2 shows heat flow versus temperature results of differential scanning calorimetry of a sample 'soft' grade sample of natural rubber/nitrile rubber/polyolefin,

Figure 3 shows loss modulus versus temperature results of dynamic mechanical analysis of a sample 'soft' grade sample of natural rubber/nitrile rubber/polyolefin,

Figure 4 shows weight loss versus temperature results of differential scanning calorimetry of a sample 'intermediate' grade sample of natural rubber/nitrile rubber/polyolefin,

Figure 5 shows heat flow versus temperature results of differential scanning calorimetry of a sample 'intermediate' grade sample of natural rubber/nitrile rubber/polyolefin,

Figure 6 shows loss modulus versus temperature results of dynamic mechanical analysis of a sample 'intermediate' grade sample of natural rubber/nitrile rubber/polyolefin,

Figure 7 shows weight loss versus temperature results of differential scanning calorimetry of a sample 'rigid' grade sample of natural rubber/nitrile rubber/polyolefin,

Figure 8 shows heat flow versus temperature results of differential scanning calorimetry of a sample 'rigid' grade sample of natural rubber/nitrile rubber/polyolefin, and

Figure 9 shows loss modulus versus temperature results of dynamic mechanical analysis of a sample 'rigid' grade sample of natural rubber/nitrile rubber/polyolefin.

DETAILED DESCRIPTION OF THE INVENTION

Described below are a number of compositions made in accordance with this invention. It will be understood that these are exemplary and that the invention is not to be limited to any one of them or to the examples collectively.

EXAMPLE 1 - *General Procedure for formation of composites*

The following is a general procedure for the formation of composites of the present invention. Quantities of individual components are given in the specific examples outlined below.

Procedure : The natural rubber is pre-masticated in an internal mixer or a mill together with the first and second compatabilisers and peptisers (if required) for about 5 minutes or less, although if a mill is used the process may take more than 10 minutes. The time is dependent upon the viscosity of the rubber. The temperature during mixing or milling preferably should not exceed 120°C. Any additives such as fillers are added during the mastication. After mixing, the stock is normally viscosity stabilised, slabbed and left to mature with polyethylene sheets between each patch. The maturation period may be 6-12 hours. The rubber matrix is then cut into strips and added to a Branbury mixer or mixer extruder (e.g. twin screw with dosing system) at between 130°C and 205°C depending on the melt temperature of the thermoplastic. The thermoplastics are then added and in teh case of a Branbury mixer after mixing for 5 minutes an antioxidant is added and after a further 1 minute the resulting composite is fed onto an extruder in a hot condition and extruded and pelletised. The product is then extruded and pelletised on a strand pelletiser or a die face cutter.

EXAMPLE 2.1 - *Rubber thermoplastic compositions with nitrile first compatabiliser and polyamide thermoplastics*

The composites in Table 1 were made according to the procedure of Example 1.

Table 1

NR	NIR / NBR	PA-6	PVA	Phenolic resin	Tin Chloride	Zinc Stearate	HVA_2	DCP	Anti oxidant
5	25	70	5	5	0.5	1	0.75	0.05	1
10	30	60	5	5	0.5	1	0.75	0.06	1
20	30	50	5	5	0.5	1	0.75	0.07	1
30	30	40	5	5	0.5	1	0.75	0.08	1
40	30	30	5	5	0.5	1	0.75	0.09	1

NR	Natural Rubber : SMRCV/ISNRCV or equivalent with low dirt content
NIR/NBR	Acrylonitrile isoprene rubber with a nitrile content of 40% or acrylonitrile butadiene rubber with a nitrile content of 40% or a 50:50 ratio of them.
PA-6	Polycaprolactam (Nylon-6) : mfi 3, shore hardness 80A.
PVA	Polyvinyl acetate
Phenolic resin	Phenolic formaldehyde resin for heat stability/hardness (Hylak; Bakelite)
Tin chloride	Stannous (II) chloride : a selection from commercial grades available
Zinc stearate	Commercial grade
HVA_2	Bismalemide (DuPont)
DCP	Dicumyl peroxide (Akzo Perkadox 14 S)v
Antioxidant:	Wingstay 100 (Goodyear)

Dehydrated castor oil (DCO) may also be added if a plasticiser is required.

EXAMPLE 2.2 - *Rubber thermoplastic compositions with nitrile first compatabiliser and polyolefin thermoplastics*

The composites in Tables 2 and 3 were made as described below.

Table 2 Soft grades

Shore Hardness	NR	NBR	LLDPE	EVA	Engage	HVA_2	Peroxide	MBTS	Zinc stearate	Anti Oxidants
65A	15	30	10	35	10	0.75	0.07	0.25	1	1
60A	15	30	10	30	15	0.75	0.07	0.25	1	1
55A	15	30	5	25	20	0.75	0.075	0.25	1	1
50A	15	30	5	20	25	0.75	0.075	0.25	1	1
45A	15	30	5	10	30	0.75	0.08	0.25	1	1
40A	15	30	5	5	35	0.75	0.08	0.25	1	1

Table 3 Intermediate grades

Shore Hardness	NR	NIR / NBR	HDPE	EVA	LLDPE	HVA_2	Peroxide	MBTS	Zinc Stearate	Anti oxidants
90A	15	25	40	20		0.75	0.06	0.25	1	1
85A	15	25	30	25	5	0.75	0.06	0.25	1	1
80A	20	30	20	20	10	0.75	0.07	0.25	1	1
75A	20	30	10	20	20	0.75	0.07	0.25	1	1
70A	25	35	5	10	25	0.75	0.08	0.25	1	1
65A	25	35		10	30	0.75	0.08	0.25	1	1

NR	Natural Rubber : SMRCV/ISNRCV or equivalent with low dirt content
NIR/NBR	Acrylonitrile isoprene rubber with a nitrile content of 40% or acrylonitrile butadiene rubber with a nitrile content of 40% or a 50:50 ratio of them.
HDPE	High Density polyethylene : melt flow index (mfi) 3; moulding grade.
EVA	Ethylene vinyl acetate : preferred grade 28% vinyl acetate content; mfi 2
LLDPE	Linear low density polyethylene : moulding grade; mfi 3 (Exxon)
Engage	Ethylene propylene plastic
HVA_2	Bismalemide (DuPont)
Peroxide	Isopropyl benzene peroxide (EIFATO Therm/AKZO Nobel)
Antioxidant:	Wingstay 100 (Goodyear)

Process:

NR, NIR and/or NBR, HDPE and EVA were masticated in a Barbender mixer at 80 rpm and 100°C. The masticated rubber matrix along with LLDPE, HVA_2, peroxide and zinc stearate are blended in an internal mixer (Branbury) at 180-190°C. Antioxidant is added at the end of the blending process. The material is extruded and pelletised as in Example 1.

EXAMPLE 2.3 - *Rubber thermoplastic compositions with nitrile first compatabiliser and polyolefin thermoplastics and a bismaleimide compatabiliser*

The composites in Table 4 were made as described below.

Table 4

Shore hardness	Natural rubber	NIR / NBR	PPHP	PPCP	HMH-DPE	LDPE	HVA_2	Peroxide	Zinc Stearate	Anti oxidant
60D	3	2	40	40	15		0.75		1	1
55D	3	2		25	50	10	0.75		1	1
50D	6	4	30	30	30		0.75	0.03	1	1
45D	9	6		30	30	25	0.75	0.04	1	1
40D	12	8		30	30	20	0.75	0.05	1	1
35D	15	10		30	30	15	0.75	0.06	1	1
30D	18	12		30	20	20	0.75	0.07	1	1
25D	24	16		20	20	20	0.75	0.08	1	1
20D	30	20		20	15	15	0.75	0.08	1	1

NR	Natural Rubber : SMRLCV or ISNRLCV or equivalent; low protein and low dirt grades are preferable.
NIR/NBR	Acrylonitrile isoprene rubber with a nitrile content of 40% or acrylonitrile butadiene rubber with a nitrile content of 40% or a 50:50 ratio of them.
PPHP	Polypropylene homopolymer : mfi 3; general purpose (Shell)
PPCP	Polypropylene co-polymer : mfi 3; general purpose (Shell)
HMHDPE	High molecular weight high density polyethylene : mfi 2 (Exxon)
LDPE	Low density polyethylene : general purpose; mfi 2 (Exxon)
HVA_2	Bismalemaleimide (Dupont)
Peroxide	Isopropyl benzene peroxide (Elf Atochem/AKZO Nobel) - should be added to run while masticating
Zinc stearate	a selection from commercial grades available
Anti-oxidant	Wingstay L/100 (Goodyear) or Santowhite (Monsanto)

2% Titanium dioxide, carbon black or Tunivan (P) [Ciba Geigy (Novartis)] can be added for additional UV protection.

PPHP - can be substituted by PPCP, PPHP to balance mould shrinkage.
Vanillin (1-2 phr) of can be added to the compound for odour.
Fillers like $CaCO_3$/talc can be loaded up to 30%.

Process:

Rubbers are masticated with 10 parts of paraffinic oils, 0.08 parts of Renacit-11 (Bayer) and/or 0.04 parts of DCO (Dehydrated Castor oil). The masticated rubber along with polyolefins, HVA_2, peroxide and zinc stearate are blended in an internal mixer at 180-190°C. Antioxidant is added at the end of the blending process. The same material is extruded and pelletised according to Example 1. It is desired that the material is allowed to expand to the maximum to avoid future mould shrinkage.

<u>EXAMPLE 3.1</u> - *Compositions and properties of rubber thermoplastic polyamide composites with nitrile based first compatabiliser*

Component	*Amount (kg)*	*Amount (kg)*	*Source/grade*	
Natural rubber	20	30	SMR-LCV Malaysia	
Nitrile butadiene rubber	20	30	JSR-N ACN content 50%; Japan	
Polyamide-6	60	40	Polycaprolactam SRF MFI 3	
Polyvinyl acetate	5	5	Commercial	
Dimethylol phenol	1	1	SP1045: Schenectady Chemicals	
Tin chloride	1	1	Commercial	
Zinc stearate	2	2	Commercial	
Bismaleimide	1	1	HVA2: DuPont (USA)	
Peroxide	0.4	0.6	t-Butylisopropyl benzene; (Perkadox 14-40A, Akzo Nobel)	
Dehydrated castor oil	0.8	1.0	Generic	
Antioxidant	2	2	Wingstay-100 (Goodyear)	
Properties			*Units*	*Test Method*
Shore Hardness	70 D	50 D	-	ASTM D 2240
Density	1.14	1.12	gm/cc	ASTM D 792
Tensile Strength	780	670	kg/cm^2	ASTM D 638
Elongation at Break	350	380	%	ASTM D 638
Flexural Modulus	2400	2000	kg/cm^2	ASTM D 638
Brittle Point	-40	-40	℃	ASTM D 746
Impact Strength	34	NB	$kg.cm/cm^2$	ASTM D 256
Heat Deflection Temp ($4.6\ kg/cm^2$)	>160	>160	℃	ASTM D 648

EXAMPLE 3.2 - *Compositions and properties of rubber thermoplastic polyester composites with nitrile based first compatabiliser*

Component	*Amount (kg)*	*Amount (kg)*	*Source/grade*	
Natural rubber	20	20	SMR-LCV Malaysia	
Nitrile butadiene rubber	20	20	JSR-N ACN content 50%; Japan	
Ethylene acrylate rubber	-	20	VAMAC (DuPont)	
Polyester (Cellulose)	60	40	Eastacel (Eastmann Chemical Products, USA)	
Polyvinyl acetate	5	5	Generic	
Dimethylol phenol	1	1	SP1045 (Schenectady Chemicals)	
Phenol formaldehyde	3	3	Hylak (Hylan Bakelite)	
Tin chloride	1	1	Commercial	
Zinc stearate	2	-	Commercial	
Bismaleimide	1	1	HVA2: DuPont (USA)	
Zinc oxide	0.6	0.5	Generic	
Dehydrated castor oil	0.8	1.0	Generic	
Antioxidant	1	1	Wingstay-100 (Goodyear)	
Properties			*Units*	*Test Method*
Shore Hardness	60 D	40 D	-	ASTM D 2240
Density	1.20	1.18	gm/cc	ASTM D 792
Tensile Strength	480	420	kg/cm^2	ASTM D 638
Elongation at Break	250	270	%	ASTM D 638
Flexural Modulus	-	-	kg/cm^2	ASTM D 638
Brittle Point	-30	-30	°C	ASTM D 746
Impact Strength	13.5	15.5	kg.cm/cm	ASTM D 256
Heat Deflection Temp ($4.6\ kg/cm^2$)	>180	>180	°C	ASTM D 648

<u>EXAMPLE 3.3</u>- *Compositions and properties of rubber thermoplastic polyurethane composites with nitrile based first compatabiliser*

Component	*Amount (kg)*	*Amount (kg)*	*Source/grade*	
Natural rubber	20	20	SMR-LCV Malaysia	
Nitrile butadiene rubber	20	20	JSR-N ACN content 50%; Japan	
Polychloroprene	-	20	Neoprene (DuPont)	
Thermpolastic polyurethane	60	40	Despiopan (Bayer); Hardness 30 Shore D	
Polyvinyl acetate	5	-	Generic	
Polyvinyl chloride	-	5	Occidental; paste grade compound	
Phenol formaldehyde	3	3	Hylak (Hylan Bakelite)	
Dimethylol phenol	1	1	SP1045 (Schenectady Chemicals)	
Tin chloride	1	-	Commercial	
Zinc stearate	2	-	Commercial	
Bismaleimide	1	1	HVA2; DuPont (USA)	
Zinc oxide	-	5	Commercial	
Peroxide	0.4	-	Dicumyl peroxide (Akzo Nobel)	
Dehydrated castor oil	0.8	1.0	Generic	
Antioxidant	2	2	Wingstay-100 (Goodyear)	
Properties			*Units*	*Test Method*
Shore Hardness	90 A	80 A	-	ASTM D 2240
Density	1.20	1.18* (1.28)	gm/cc	ASTM D 792
Tensile Strength	520	460	kg/cm^2	ASTM D 638
Elongation at Break	400	480	%	ASTM D 638
Flexural Modulus	-	-	kg/cm^2	ASTM D 638
Brittle Point	-50	-50	°C	ASTM D 746
Impact Strength	NB	NB	kg.cm/cm^2	ASTM D 256
Heat Deflection Temp (4.6 kg/cm^2)	NA	NA	°C	ASTM D 648

NB - No break; NA - Not applicable

* density given is measured by displacement, and value in brackets are empirical values

EXAMPLE 3.4 - *Compositions and properties of rubber thermoplastic polyolefin composites with nitrile based first compatabiliser*

Component	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Source/grade*
Natural rubber	3	9	18	25	30	15	SMR-LCV Malaysia
Nitrile butadiene rubber	-	2	6	20	20	15	JSR-N ACN content 50%; Japan
Chlorinated polyethylene	-	-	-	-	15	15	
EPDM	1	2	3	-	-	-	JSR; Low viscocity; low ethylene content
Magnesium oxide	-	-	-	-	5	5	Commercial
Epoxidised natural rubber	1	2	3	5	-	-	Epoxide level 50%; Guthrie (Malaysia)
Polypropylene homopolymer	40	-	-	-	-	-	Shell; mfi 3
Polypropylene copolymer	40	30	30	-	-	-	Shell; mfi 4
Low density polyethylene	-	25	20	-	-	-	
Linear low density polyethylene	-	-	-	20	10	5	Exxon
Engage	-	-	-	-	10	25	DuPont
Zinc stearate	2	2	2	3	3	3	Commercial
Bismaleimide	0.75	0.75	0.75	0.75	0.75	0.75	HVA2; DuPont (USA)
Peroxide	–	0.04	0.07	0.08	0.08	0.8	PERKADOX 14-40A (Akzo Nobel)

Chlorinated paraffin oil	_	2	4	7	7	5	Commercial	
Antioxidant	2	2	3	3	3	3	Wingstay-100 (Goodyear)	
Properties							*Units*	*Test Method*
Shore Hardness	60 D	45 D	90 A	75 A	65 A	50 A	-	ASTM D 2240
Density	0.91	0.92	0.93	0.97	0.97	0.98	gm/cc	ASTM D 792
Ultimate tensile strength	24	16	12	9	7.9	4.8	MPa	ASTM D 638
Ultimate elongation	550	450	374	480	460	358	%	ASTM D 638
Tear strength	102.6	76.1	44.7	28.3	32.6	25.5	N/mm	
100% Modulus	14.1	11.9	6.5	3.1	3.4	1.9	MPa	ASTM D 638
Brittle Point	-52.5	-57.5	-57.5	-57.5	-60	-60	°C	ASTM D 746
Abrasion resistance	115	95	60	84	47	60	mg/ 1000 rev	Tabor test
Impact Strength	30	35	NA	NA	NA	NA	kg.cm/ cm^2	ASTM D 256
Heat Deflection Temp (4.6 kg/cm^2)	130	130	120	NA	NA	NA	°C	ASTM D 648

<u>EXAMPLE 4</u> - *Compositions and properties of rubber thermoplastic composites with nitrile and acrylate based first compatabilisers*

Component	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Source/grade*
Natural rubber	25	25	25	25	SMR-LCV Malaysia
Nitrile butadiene rubber	15	15	15	-	JSR-N ACN content 50%; Japan
Ethylene acrylate rubber	10	10	10	10	Vamac; DuPont
Polychloroprene	-	-	-	15	Neoprene; DuPont
Polyvinyl acetate	5	5	5	-	Generic
Polyamide	-	45	-	-	PA-6; mfi 3
Thermoplastic urethane	-	-	45	45	Bayer; Hardness 80A
Polymethyl methacrylate	45	-	-	-	PMMA; Moulding grade
Polyvinyl chloride	-	-	-	5	Compound paste grade; Occidental
Dehydrated castor oil	2	2	2	-	Generic
Chlorinated paraffin oil	-	-	-	3	Commercial
Zinc stearate	2	2	2	2	Commercial
TMTD	0.1	0.1	0.1	0.1	Thiurad (Monsanto)
Magnesium oxide	4	4	4	4	Commercial
Phenolic resin	1	1	1	0.5	SP1045; Schenectady
Acrylamide	0.5	0.5	0.5	-	Commercial
Antioxidant	2	2	2	2	Wingstay-100 (Goodyear)
Properties					*Units*
Shore Hardness	90 A	80 A	60 A	60 A	-
Density	1.01	1.02	1.04	1.24*	gm/cc
Tensile strength	410	430	380	380	kg/cm^2
Elongation at break	300	380	420	420	%
Tension set	33	31	29	28	%

* empirical values

<u>EXAMPLE 5</u>- *Compositions and properties of rubber thermoplastic composites with chlorine based first compatabilisers*

Component	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Source/grade*
Natural rubber	25	25	25	25	SMR-LCV Malaysia
Polychloroprene	25	25	15	15	Neoprene: DuPont
Chlorinated polyethylene	-	-	10	-	Bayer CM
Chlorosulphonated polyethylene	-	-	-	10	Hypalon; DuPont
Ethylene vinyl acetate	-	-	5	5	Mitsui DuPont
Polyvinyl chloride	5	35	-	-	Compound: 70 Shore A hardness
Thermoplastic urethane	45	15	-	-	Bayer; 80 Shore A
Low density polyethylene	-	-	45	45	mfi 5 moulding grade
Phenolic resin	2	2	2	2	SP1045; Schenectady
Zinc stearate	3	3	3	3	Commercial
Bismaleimide	0.3	0.3	0.3	0.3	HVA2:DuPont
Magnesium oxide	5	5	5	5	Commercial
Chlorinated paraffin oil	3	3	3	3	Commercial
Antioxidant	2	2	2	2	Wingstay-100 (Goodyear)
Properties					*Units*
Shore Hardness	60 A	55 A	80 A	80 A	-
Density	1.20*	1.20*	1.8*	1.8*	gm/cc
Tension set	28	32	33	32	%
Elongation at break	430	410	380	360	%

* empirical values

<u>EXAMPLE 6</u>- *Compositions and properties of rubber thermoplastic composites with epoxide based first compatabilisers*

Component	*Amount (kg)*	*Amount (kg)*	*Amount (kg)*	*Source/grade*
Natural rubber	25	25	50	SMR-LCV Malaysia
Epoxidised natural rubber	25	30	-	ENR at 50% epoxy levels
EVA	10	10	10	Mitsui DuPont
Polypropylene copolymer	40	40	40	Shell KMT 6100; mfi 4
Bismaleimide	1	1	1	HVA_2; DuPont
Peroxide	0.06	0.06	0.06	Perkadox 14S (Akzo Nobel)
Naphthalic oil	3	3	3	Commercial
Antioxidant	1	1	1	Wingstay-100 (Goodyear)
Properties				*Units*
Shore Hardness	80 A	85 A	80 A	-
Density	0.93	0.93	0.93	gm/cc
Tensile strength	490	510	490	kg/cm^2
Tension set	30	30	27	%
Elongation at break	380	400	400	%

EXAMPLE 7- *Properties of rubber thermoplastic composition with nitrile first compatabiliser and polyolefin thermoplastics*

A 'soft' grade composition comprising:
natural rubber (15 parts),
nitrile butadiene rubber (30 parts),
linear low density polyethylene (5 parts),
ethylvinyl acetate (25 parts),
engage (20 parts),
HVA_2 (0.75 parts),
peroxide (0.075 parts),
MBTS (0.25 parts),
zinc stearate (1 part) and
antioxidant (1 part)
was subjected to thermogravimetric analysis, differential scanning calorimetry and dynamical mechanical analysis as described.

METHODS

Thermogravimetric analysis (TGA)

T.A. Instruments TGA 2950 connected to a Thermal Analyst 2200 Controller was used to perform experiments and record the results. Prior to and during each thermogravimetric analysis, the system was purged with high purity nitrogen at a rate of 50 ml/min. Once the sample was loaded, the sample was heated with heating ramp of 5°C/min up to 600°C. Weight was recorded versus temperature on a continuous basis for analysis.

Differential scanning calorimetry (DSC)

DSC was conducted using DSC 2920 from TA Instruments. A weighed amount of sample was analysed from -100°C to 400°C under nitrogen flow, and heating rate of 10°C/min.

Dynamic mechanical analyser (DMA)

DMA was carried out using DMA 2980 (TA Instruments) operating in tension mode from -140°C to 100°C at 1 Hz frequency and 0.08% strain amplitude, at programmed heating rate of 2°C/min. Liquid nitrogen was used to achieve sub-ambient conditions. Glass transition temperature (Tg) of the samples was determined from tan∂ curves.

RESULTS

TGA: Figure 1 shows weight loss versus temperature of the sample. The results show the approximate composition of 53% rubber (PU added), 25% plastic, 13% plasticiser and 9% other material.

DSC: Figure 2 shows two melting points and two broad endothermic decompsoitions. The first metling point is broad at temperature 118°C with heat of fusion of 3.66J/g. The second melting point is at 157°C with heat of fusion of 6.47 J/g.

DMA: The glass transition temperature was selected as the peak position of the $\tan\partial$ when plotted vs temperature. From Figure 3 two sharp glass transitions can be noticed, the first at -60°C and the second glass transiton at -21°C. The graph indicates a storage modulus of 18.59 MPa at 25°C.

<u>EXAMPLE 8</u>- *Properties of rubber thermoplastic composition with nitrile first compatabiliser and polyolefin thermoplastics*

An 'intermediate' grade composition comprising:
natural rubber (20 parts),
nitrile butadiene rubber (30 parts),
high density polyethylene (10 parts),
ethylvinyl acetate (20 parts),
linear low density polyethylene (20 parts),
HVA_2 (0.75 parts),
peroxide (0.07 parts),
MBTS (0.25 parts),
zinc stearate (1 part) and
antioxidant (1 part)
was subjected to thermogravimetric analysis, differential scanning calorimetry and dynamic mechanical analysis using the methods as described in Example 7.

RESULTS

TGA: Figure 4 shows weight loss versus temperature of the sample. The results show a first step of natural rubber weight loss that is not a sharp peak and the total amount is

26% mixture of natural rubber and other rubber. A second step is the decompositions of plastics in the amount of 71% and a residue of 3%.

DSC: Figure 5 shows two melting points and two broad endothermic decompsoitions. The first metling point is at temperature 125°C with heat of fusion of 15.10J/g. The second melting point is at 162°C with heat of fusion of 36.32 J/g.

DMA: The glass transition temperature was selected as the peak position of the tan∂ when plotted vs temperature. From Figure 6 two sharp glass transitions can be noticed, the first a sharp peak at -58°C, which represents that glass transition of the natural rubber and nitrile rubber indicating their compatability. A second broad glass transiton at 0.8°C is indicative of partially miscible polyolefins. The graph indicates a storage modulus of 298.85 MPa at 25°C.

<u>EXAMPLE 9</u>- *Properties of rubber thermoplastic composition with nitrile first compatabiliser and polyolefin thermoplastics*

A 'rigid' grade composition comprising:
natural rubber (6 parts),
nitrile butadiene rubber (4 parts),
polypropylene homopolymer (30 parts),
polypropylene copolymer (30 parts),
high molecular weight high density polyethylene (30 parts)
HVA_2 (0.75 parts),
peroxide (0.03 parts),
zinc stearate (1 part) and
antioxidant (1 part)
was subjected to thermogravimetric analysis, differential scanning calorimetry and dynamic mechanical analysis using the methods as described in Example 7.

RESULTS

TGA: Figure 7 shows weight loss versus temperature of the sample. The results show a first step of natural rubber weight loss and the amount is 9% . A second step is the decompositions of polypropylene and polyethylene in the amount of 90% and a residue of 1%.

DSC: Figure 8 shows two melting points and a broad endothermic decomposition with several shoulders. The first metling point is at tempaerature 126°C with heat of fusion of 18.61J/g. The second metlting point is at 165°C with heat of fusion of 40.93 J/g.

DMA: The glass transition temperature was selected as the peak position of the tan∂ when plotted vs temperature. From Figure 9 two broad glass transitions can be noticed, the first at -52°C, and the second broad glass transiton at 9.7°C in indicative of partially miscible polyolefins. The graph indicates a storage modulus of 630 MPa at 25°C.

CLAIMS

1. A rubber matrix including :

a) 10-90% (v/v) of natural rubber

b) one or more first compatabilisers selected from a group of polymers containing either
i) a nitrile group,
ii) a halogen,
iii) an acetate group,
iv) an epoxide,
v) a styrene, or
vi) an acrylate

c) one or more second compatabilisers which are interfacial copromoters selected from a group comprising either
i) polyvinyl acetate,
ii) ethylene vinyl acetate,
iii) polyacrylonitrile or high nitrile resin,
iv) acrylamide or polyacrylamide,
v) a phenolic resin,
vi) an acrylate polymer,
vii) a halogenated polymer,
viii) maleic anhydride or polymaleic anhydride, or
ix) a bismaleimide.

2. A rubber matrix as in claim 1 wherein the first and second compatabilisers are different.

3. A rubber matrix as in claim 2 wherein the rubber matrix is suitable for mixing with at least one thermoplastic to form a thermoplastic rubber composite.

4. A rubber matrix as in claim 3 wherein the thermoplastic is selected from one or more of the group including polyolefins, polyamides, polyesters, polyurethanes, polystyrene and acrylonitrile butadiene styrene.

5. A rubber matrix as in claim 2 wherein the natural rubber has a low protein and a low dirt content.

6. A rubber matrix as in claim 5 wherein the natural rubber is selected from the list including deproteinated natural rubber, oil extended natural rubber, peptised natural rubber, superior processing rubber, standard Malaysian rubber constant viscosity, standard Malaysian rubber low viscosity, standard Malaysian rubber general purpose and Indian standard natural rubber latex constant viscosity grades.

7. A rubber matrix as in claim 6 wherein the natural rubber is standard Malaysian rubber or Indian standard natural rubber latex constant viscosity grade.

8. A rubber matrix as in claim 6 wherein the content of natural rubber in the rubber matrix is between 10 phr and 90 phr.

9. A rubber matrix as in claim 8 wherein the rubber matrix has between 20 phr to 40 phr natural rubber

10. A rubber matrix as in claim 2 wherein the nitrile based first compatabiliser is selected from the list including acrylonitrile diene rubber, nitrile natural rubber, polyacrylonitrile and high nitrile polymer.

11. A rubber matrix as in claim 10 wherein the acrylonitrile diene rubber is nitrile isoprene rubber or nitrile butadiene rubber.

12. A rubber matrix as in claim 10 wherein the amount of nitrile based compatabiliser is greater than 10% of the rubber matrix.

13. A rubber matrix as in claim 12 wherein the acrylonitrile diene rubber and nitrile natural rubber has an acrylonitrile content of over 20%.

14. A rubber matrix as in claim 2 wherein the halogenated first compatabiliser is a halogenated polymer selected from the list including chlorinated rubber, polyvinyl chloride, polychloroprene, chlorinated polyethylene/ polychloroprene, chlorosulphonated polyethylene/polychloroprene and vinyl diene fluoride.

15. A rubber matrix as in claim 14 wherein the halogenated first compatabiliser is halogenated rubber formed *in situ* by halogenation of the rubber matrix with a halogen source.

16. A rubber matrix as in claim 14 wherein the halogenated rubber is formed by the inclusion of chlorinated paraffin oil in the rubber matrix.

17. A rubber matrix as in claim 14 wherein the halogen containing polymer comprises greater than 15% of the rubber matrix.

18. A rubber matrix as in claim 2 wherein the epoxide based first compatabiliser is epoxidised natural rubber.

19. A rubber matrix as in claim 18 wherein the epoxidised natural rubber is formed *in situ* by the reaction of natural rubber with hydrogen peroxide/formic acid/acetic acid.

20. A rubber matrix as in claim 19 wherein the epoxide based compatabiliser has an epoxide content of 20 to 50% to give a rubber matrix having an epoxide content of 20 to 25%.

21. A rubber matrix as in claim 2 wherein the acetate containing first compatabiliser is selected from the list including polyvinyl acetate, ethylene-vinyl acetate and vinyl acetate rubber.

22. A rubber matrix as in claim 21 wherein the acetate polymer comprises 30 to 50% of the rubber matrix.

23. A rubber matrix as in claim 22 wherein the acetate polymer comprises 30% of the rubber matrix.

24. A rubber matrix as in claim 21 wherein the rubber matrix has a vinyl acetate content of greater than 20%.

25. A rubber matrix as in claim 2 wherein the acrylate based first compatabiliser is selected from the list including an acrylic rubber and a polymer formed from ethyl acrylate, methyl acrylate, or methyl methacrylate.

26. A rubber matrix as in claim 2 wherein the styrene based first compatabiliser is selected from the list including styrene natural rubber, styrene butadiene rubber, styrene isoprene styrene block coploymer and styrene ethyl butylene styrene block copolymer.

27. A rubber matrix as in claim 2 wherein more than one of the first compatabilisers is used in the rubber matrix.

28. A rubber matrix as in claim 27 wherein a halogenated compatabiliser is used in conjunction with a nitrile compatabiliser.

29. A rubber matrix as in claim 27 wherein an acrylate compatabiliser is used in conjunction with a nitrile compatabiliser.

30. A natural rubber thermoplastics composite including:

a) 10-90% (v/v) of natural rubber

b) one or more first compatabilisers selected from a group of polymers containing either
   i) a nitrile group,
   ii) a halogen,
   iii) an acetate group,
   iv) an epoxide,
   v) a styrene, or
   vi) an acrylate

c) one or more second compatabilisers which are interfacial copromoters selected from a group comprising either
   i) polyvinyl acetate,
   ii) ethylene vinyl acetate,
   iii) polyacrylonitrile or high nitrile resin,
   iv) acrylamide or polyacrylamide,

v) a phenolic resin,
vi) an acrylate polymer,
vii) a halogenated polymer,
viii) maleic anhydride or polymaleic anhydride, or
ix) a bismaleimide

d) one or more thermopolastics selected from a group comprising either
i) polyurethanes,
ii) polyesters,
iii) polyamides,
iv) acrylates,
v) acrylonitrile butadiene styrene,
vi) polyolefins, or
vii) cellulose esters.

31. A natural rubber thermoplastics composite as in claim 30 wherein two phases are formed, a rubber matrix including a) to c) as a rubber phase, and a thermoplastics component in a plastics phase, and the ratio of rubber phase to plastic phase is between 5:95 and 90:10.

32. A natural rubber thermoplastics composite as in claim 31 wherein the thermoplastic rubber composite can be recycled, reprocessed, and/or re-moulded.

33. A natural rubber thermoplastics composite as in claim 31 wherein a soft composite is formed by compounding the rubber matrix with polyolefins, polyvinyls or polyurethanes.

34. A rubber matrix as in claim 33 wherein the plastics are selected from the group including polypropylene, polyethylene, polyvinyl acetate, ethylene vinyl acetate, ethylene propylene plastic (Engage; DuPont), polyurethanes or polyvinyl chloride.

35. A natural rubber thermoplastics composite as in claim 34 wherein the natural rubber content in the rubber matrix is preferably about 30-70%, and the rubber matrix and plastics are blended in relative proportions of 5-70 parts to 95-30 parts to a total of 100 parts respectively.

36. A natural rubber thermoplastics composite as in claim 31 wherein an intermediate composite is formed by compounding the rubber matrix with polyurethanes, polyamides, polyvinyls or polyesters.

37. A natural rubber thermoplastics composite as in claim 31 wherein a rigid composite is formed by compounding the rubber matrix with polyolefins, polyurethanes or polyamides.

38. A natural rubber thermoplastics composite as in claim 31 wherein the thermoplastic polyolefin is selected from the group including high density polyethylene, linear low density polyethylene, polypropylene homo polymer, polyproylene copolymer and poly(ethylene-co-propylene).

39. A natural rubber thermoplastics composite as in claim 31 wherein the thermoplastic polyamide is a crystalline or resinous high molecular weight copolymer or terpolymer.

40. A natural rubber thermoplastics composite as in claim 31 wherein the thermoplastic polyamide is chosen form the list including polycaprolactam (Nylon-6), polylauryllactam (Nylon-12), polyhexamethyleneadipamide (Nylon-6,6), polyhexamethyleneazelamide (Nylon-6,9), polyhexamethylenesebacamide (Nylon-6,10), polyhexamethyleneisophthalamide (Nylon-6,IP) and the condensation product of 11-aminoundecanoic acid (Nylon-11).

41. A natural rubber thermoplastics composite as in claim 31 wherein the thermoplastic polyurethane is a thermoplastic polyurethane resin based on caprolactam and having a Shore A hardness of 80 to 90.

42. A natural rubber thermoplastics composite as in claim 31 wherein the thermoplastic polyester is a thermoplastic polyester prepared by condensation of one or more dicarboxylic acids, anhydrides or esters and one or more diol.

43. A natural rubber thermoplastics composite as in claim 31 wherein the thermoplastic polyester is a cellulosic polyester.

44. A natural rubber thermoplastics composite as in claim 43 wherein the cellulosic polyester is selected from the list including polymers of cellulose acetate, cellulose acetobutyrate and cellulose propionate.

45. A natural rubber thermoplastics composite as in claim 31 wherein the polyester is a polycarbonate.

46. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains a nitrile based first compatabiliser, a polyvinyl acetate second compatabiliser and a polyamide thermoplastic.

47. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains a nitrile based first compatabiliser, an ethylene vinyl acetate second compatabiliser and a polyolefin thermoplastic.

48. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains a nitrile based first compatabiliser, a chlorinated polyethylene second compatabiliser and a polyolefin thermoplastic.

49. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains a nitrile based first compatabiliser, a polyvinyl acetate second compatabiliser and a polyester thermoplastic.

50. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains a nitrile based first compatabiliser, a polyvinyl acetate second compatabiliser and a polyurethane thermoplastic.

51. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains a nitrile based first compatabiliser, a polyvinyl chloride second compatabiliser and a polyurethane thermoplastic.

52. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains an epoxide based first compatabiliser, a bismaleimide second compatabiliser and a polyolefin thermoplastic.

53. A natural rubber thermoplastics composite as in claim 31 wherein the rubber matrix contains an acrylate based first compatabiliser, a polychloroprene second compatabiliser and a polyurethane thermoplastic.

54. A natural rubber thermoplastics composite as in claim 31 wherein the composite includes a curative agent added at the time of mixing of the rubber matrix with the plastics phase.

55. A natural rubber thermoplastics composite as in claim 54 wherein the curative system is selected from the group including a dimethylol phenol system, a bismaleimide system, a bismaleimide MBTS system, a bismaleimide peroxide system, an organic peroxide system, an accelerated sulphur system, a urethane system, a borane system and a radiation system.

56. A natural rubber thermoplastics composite as in claim 54 wherein the curative agent includes an interfacial promoter.

57. A natural rubber thermoplastics composite as in claim 56 wherein the interfacial promoter is selected from the list including phenylene bismaleimide, ethylene glycol dimethacrylate, trimethylo propane trimethacrylate, triallyl isocyanourate and triallyl cyanourate.

58. A natural rubber thermoplastics composite as in claim 31 wherein the properties of the composite are modified by the inclusion of one or more additives.

59. A natural rubber thermoplastics composite as in claim 58 wherein the additive is selected from the list including heat stabilising chemicals, flame retarding chemicals, peptising agents, fillers, extenders, plasticisers, pigments, accelerators, stabilisers, antidegradants, anti-oxidants, UV filters, processing aids and extender oils.

60. A natural rubber thermoplastics composite as in claim 59 wherein at least part of the thermoplastic used in the composite is derived from recycled thermoplastics.

61. An article made from the natural rubber thermoplastics composite of claim 30, wherein the article is formed by extrusion, injection moulding or compression moulding.

62. A method of forming a natural rubber thermoplastics composite, the method including the steps of:

forming a rubber matrix, said matrix including

a) 10-90% (v/v) of natural rubber

b) one or more first compatabilisers selected from a group of polymers containing either
   - i) a nitrile group,
   - ii) a halogen,
   - iii) an acetate group,
   - iv) an epoxide,
   - v) a styrene, or
   - vi) an acrylate

c) one or more second compatabilisers which are interfacial copromoters selected from a group comprising either
   - i) polyvinyl acetate,
   - ii) ethylene vinyl acetate,
   - iii) polyacrylonitrile or high nitrile resin,
   - iv) acrylamide or polyacrylamide,
   - v) a phenolic resin,
   - vi) an acrylate polymer,
   - vii) a halogenated polymer,
   - viii) maleic anhydride or polymaleic anhydride, or
   - ix) a bismaleimide, and

combining the rubber matrix with a plastics phase, said plastics phase including one or more thermopolastics selected from a group comprising either

- i) polyurethanes,
- ii) polyesters,
- iii) polyamides,
- iv) acrylates,
- v) acrylonitrile butadiene styrene,
- vi) polyolefins, or
- vii) cellulose esters.

63. A method of forming a natural rubber thermoplastics composite as in claim 62 wherein additives are added to the rubber matrix.

64. A method of forming a natural rubber thermoplastics composite as in claim 63 wherein the rubber matrix is formed in a cold mixing process.

65. A method of forming a natural rubber thermoplastics composite as in claim 64 wherein the cold mixing process is performed at a temperature of less than about 120°C.

66. A method of forming a natural rubber thermoplastics composite as in claim 65 wherein the rubber phase is viscosity stabilised and left to mature after mixing and before being combined with the plastics phase.

67. A method of forming a natural rubber thermoplastics composite as in claim 66 wherein the rubber matrix and the plastics phase are combined using melt mixing or dynamic vulcanisation.

68. A method of forming a natural rubber thermoplastics composite as in claim 67 wherein the composite is formed by mixing the plastics phase and the rubber matrix and masticating the mix at a temperature sufficient to at least soften the plastic.

69. A method of forming a natural rubber thermoplastics composite as in claim 68 wherein the thermoplastic composition is formed by mixing the plastics phase and the rubber matrix and masticating the mix at a temperature above the melting point of the plastic.

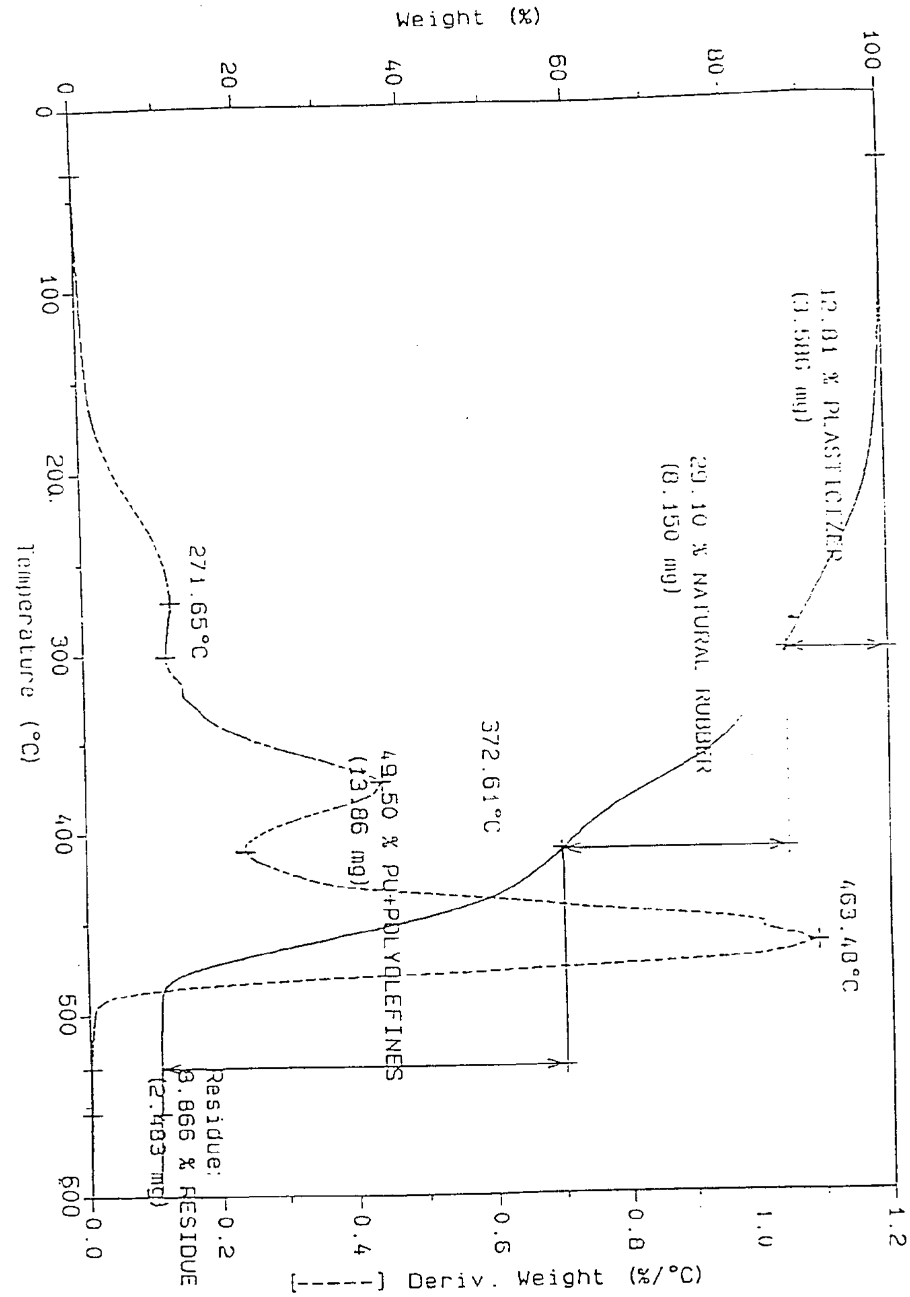
Weight (%)
29.10 % NATURAL RUBBER
(8.150 mg)
49.50 % PU+POLYOLEFINES
(13.86 mg)
Residue:
8.866 % RESIDUE
271.65°C
372.61°C
463.48°C
Temperature (°C)
[-----] Deriv. Weight (%/°C)

FIGURE 1

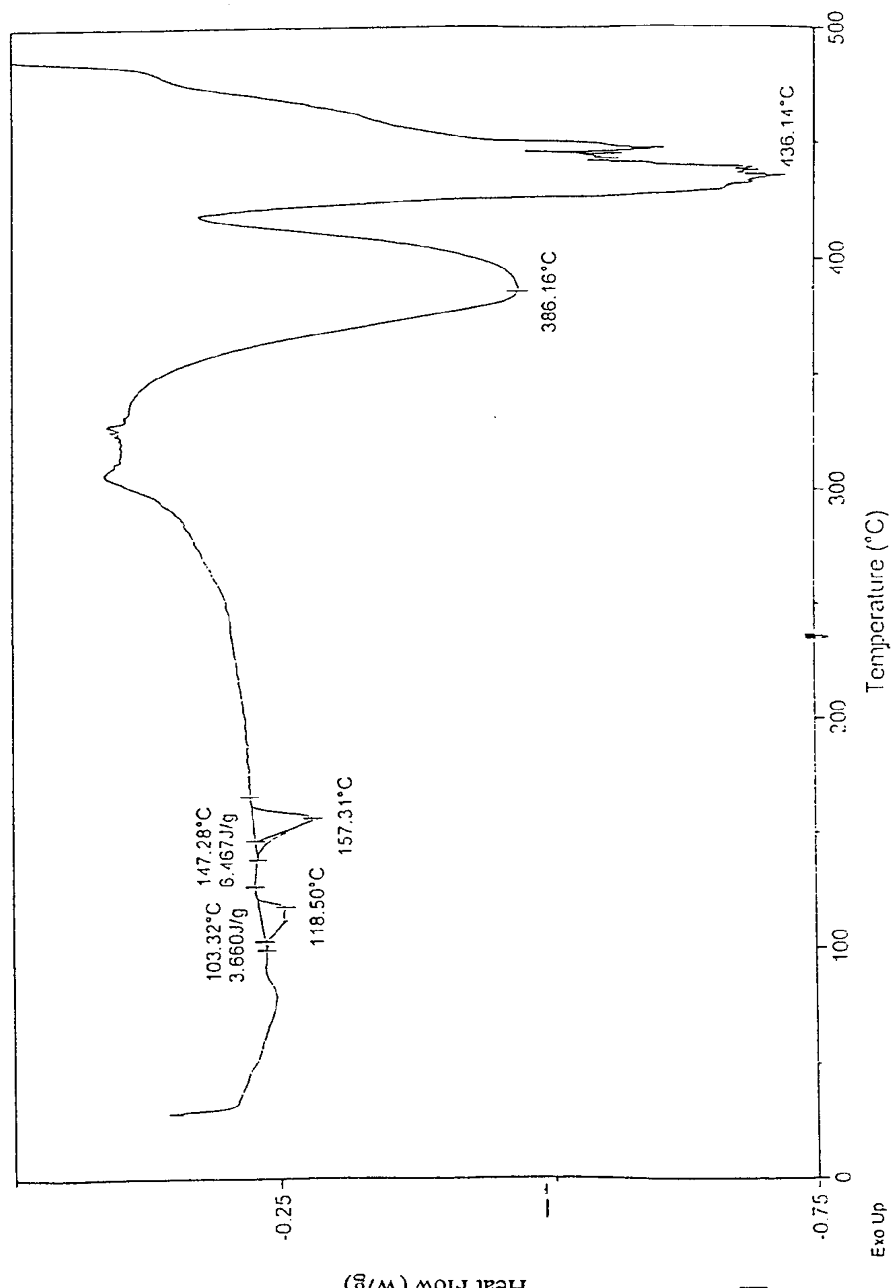
436.14°C
386.16°C
147.28°C
6.467J/g
157.31°C
103.32°C
3.660J/g
118.50°C
Temperature (°C)
Heat Flow (W/g)
Exo Up
-0.25
-0.75
0
100
200
300
400
500

FIGURE 2

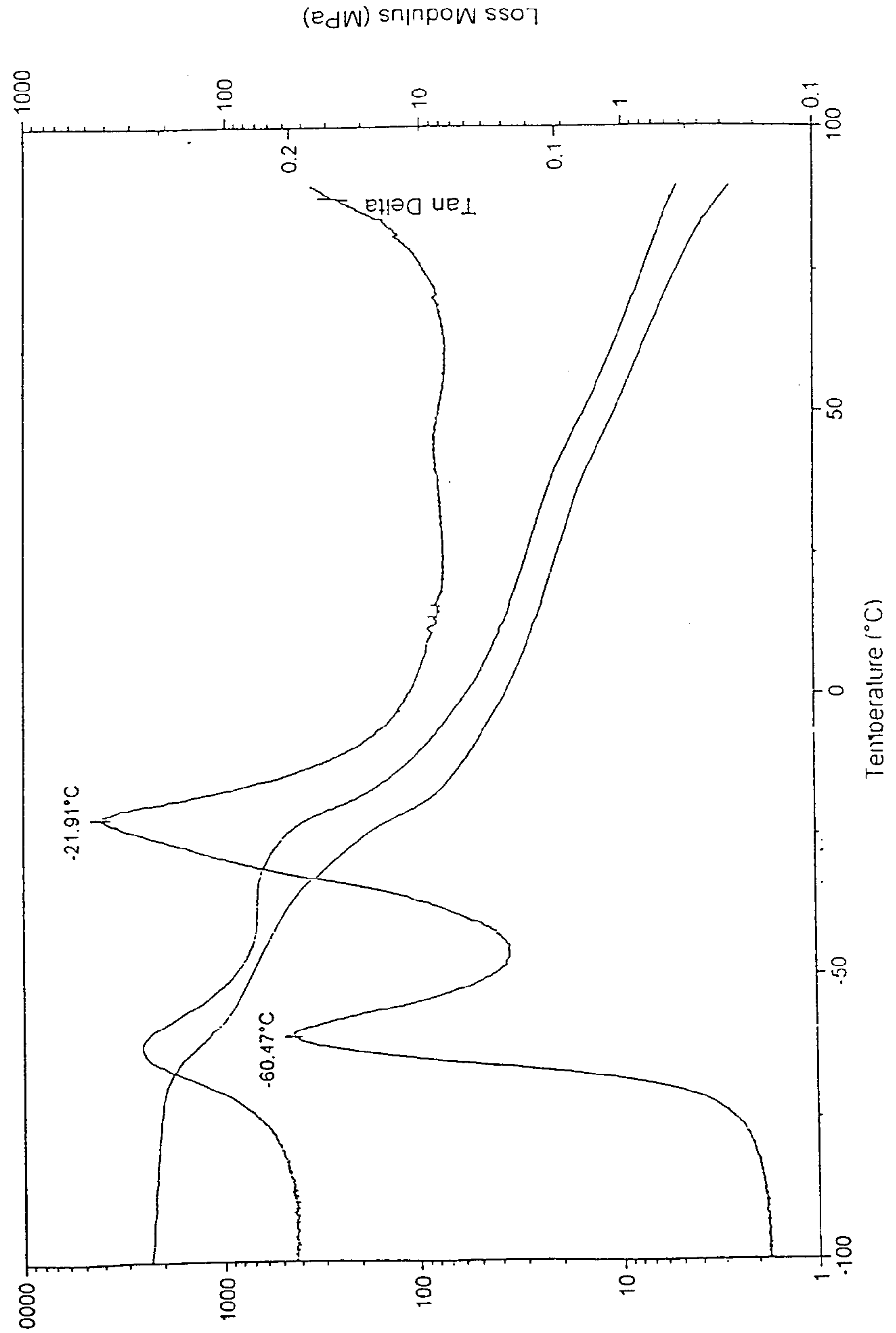
Loss Modulus (MPa)
1000
100
10
1
0.1
0.2
0.1
Tan Delta
-21.91°C
-60.47°C
-100
-50
0
50
100
Temperature (°C)
10000
1000
100
10
1
Storage Modulus (MPa)

FIGURE 3

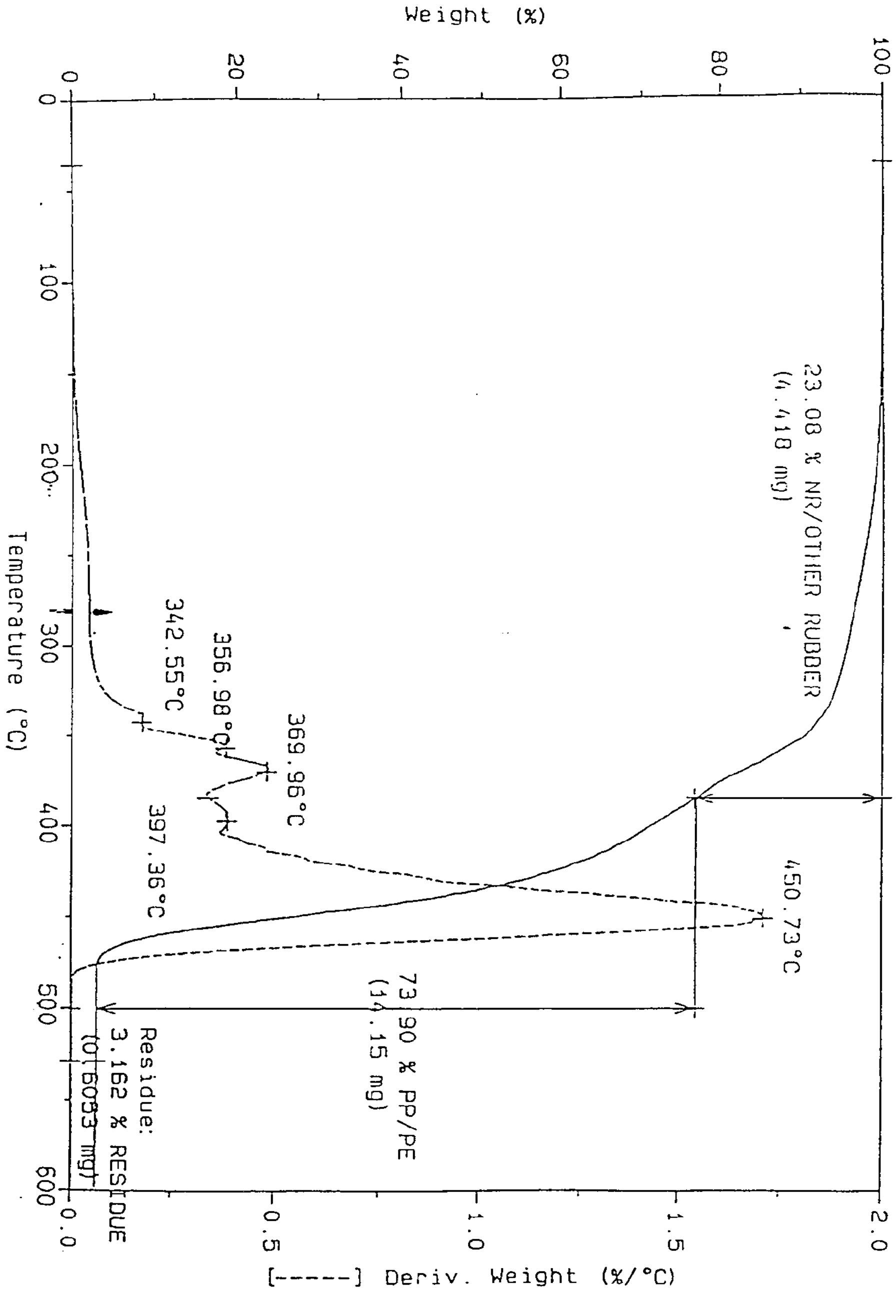
Weight (%)
0
20
40
60
80
100
0
100
200
300
400
500
600
Temperature (°C)
23.08 % NR/OTHER RUBBER
(4.418 mg)
342.55°C
356.98°C
369.96°C
397.36°C
450.73°C
73.90 % PP/PE
(14.15 mg)
Residue:
3.162 % RESIDUE
(0.6053 mg)
0.0
0.5
1.0
1.5
2.0
[-----] Deriv. Weight (%/°C)

FIGURE 4

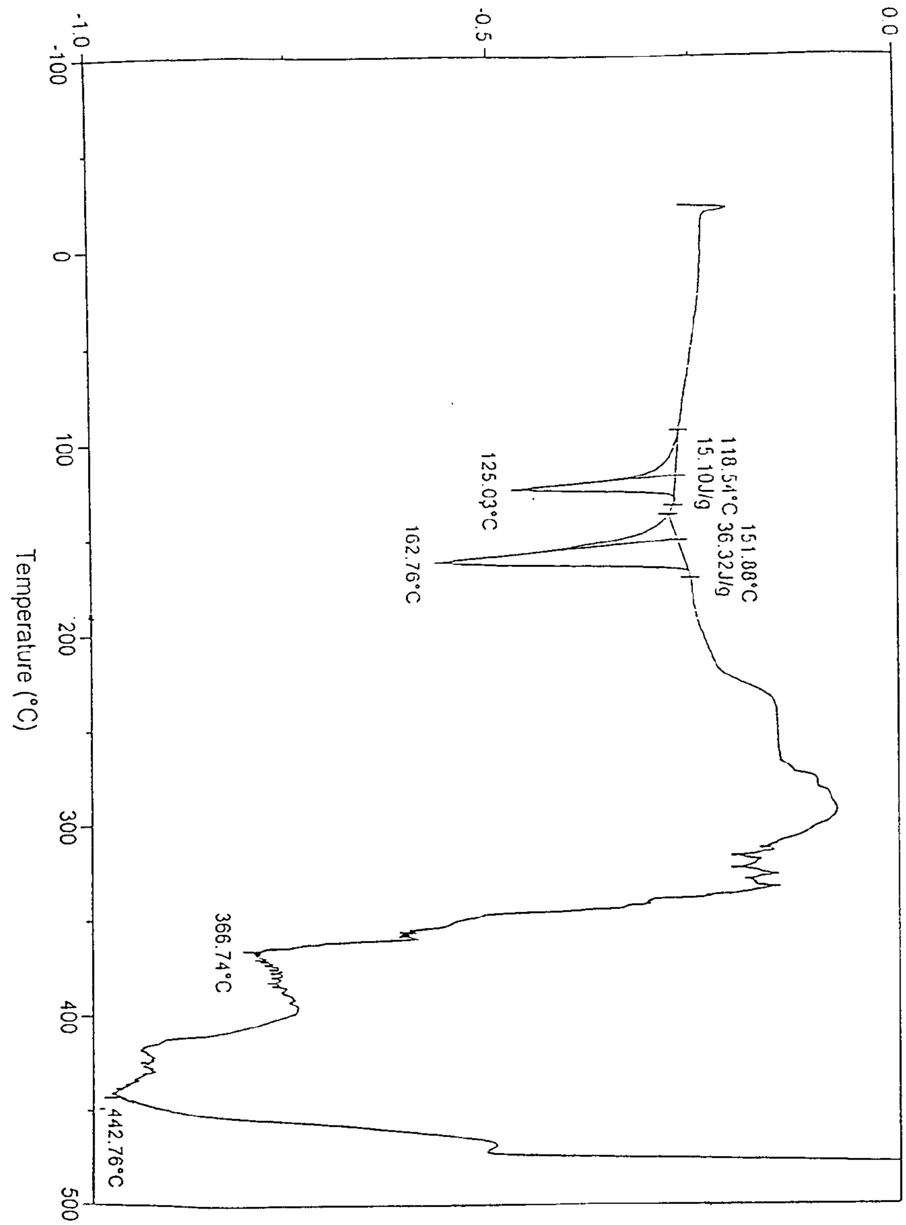
0.0
-0.5
-1.0
-100
0
100
200
300
400
500
Temperature (°C)
118.54°C
15.10J/g
125.03°C
151.88°C
36.32J/g
162.76°C
366.74°C
442.76°C

FIGURE 5

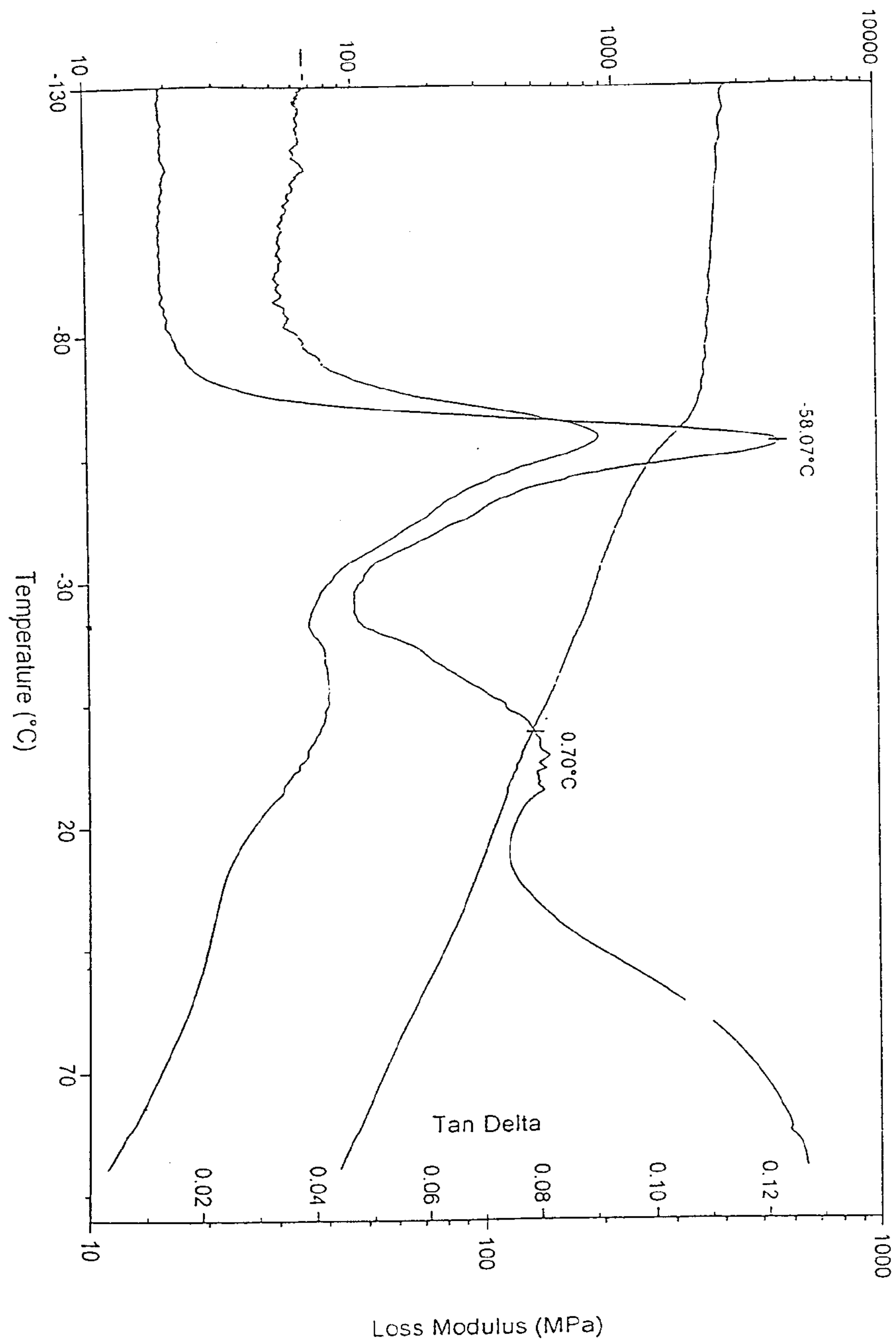
-58.07°C
0.70°C
Temperature (°C)
-130
-80
-30
20
70
10
100
1000
10000
Tan Delta
0.02
0.04
0.06
0.08
0.10
0.12
Loss Modulus (MPa)

FIGURE 6

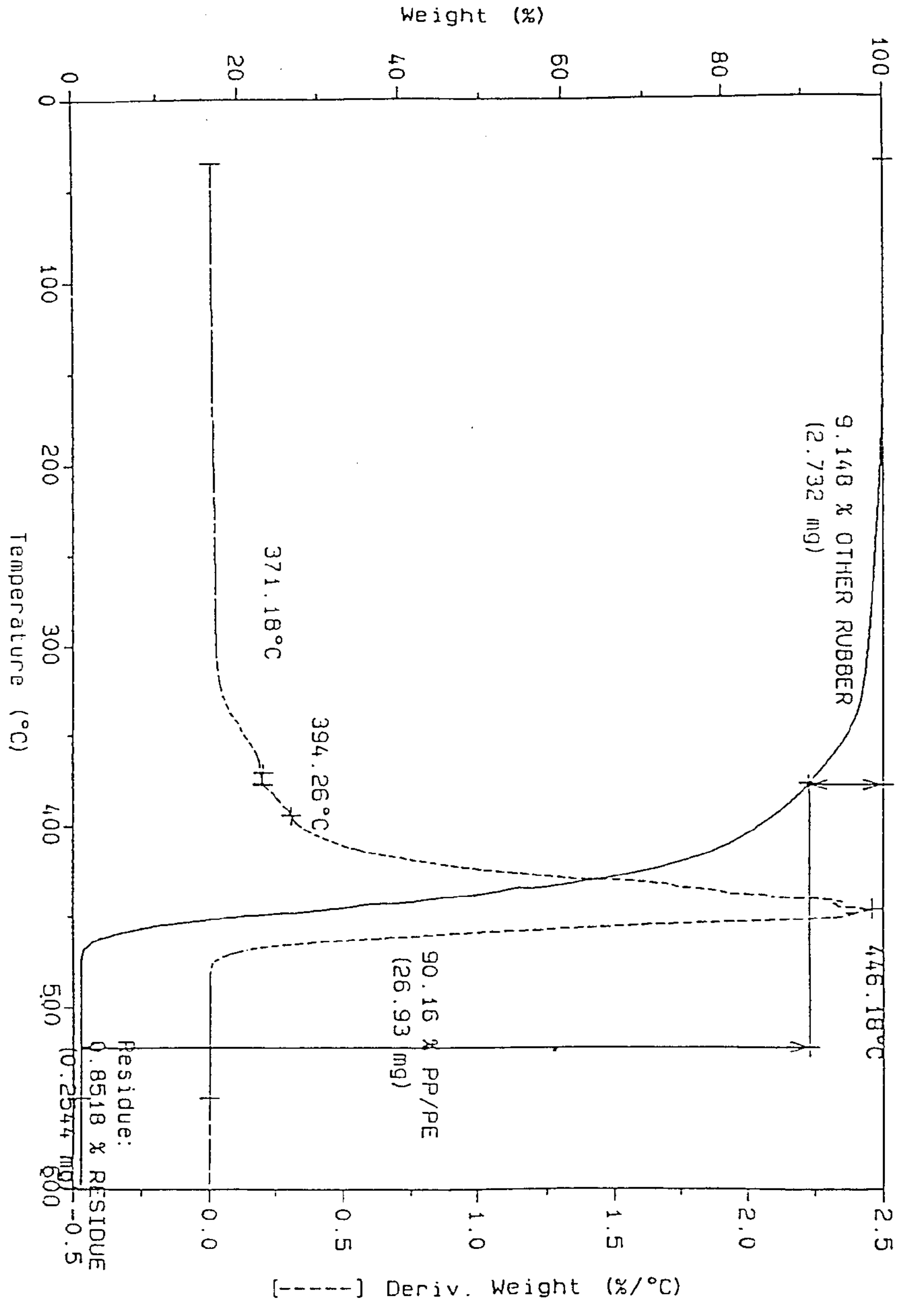
Weight (%)
Temperature (°C)
[-----] Deriv. Weight (%/°C)
9.148 % OTHER RUBBER
(2.732 mg)
371.18°C
394.26°C
446.18°C
90.16 % PP/PE
(26.93 mg)
Residue:
0.8518 % RESIDUE
(0.2544 mg)

FIGURE 7

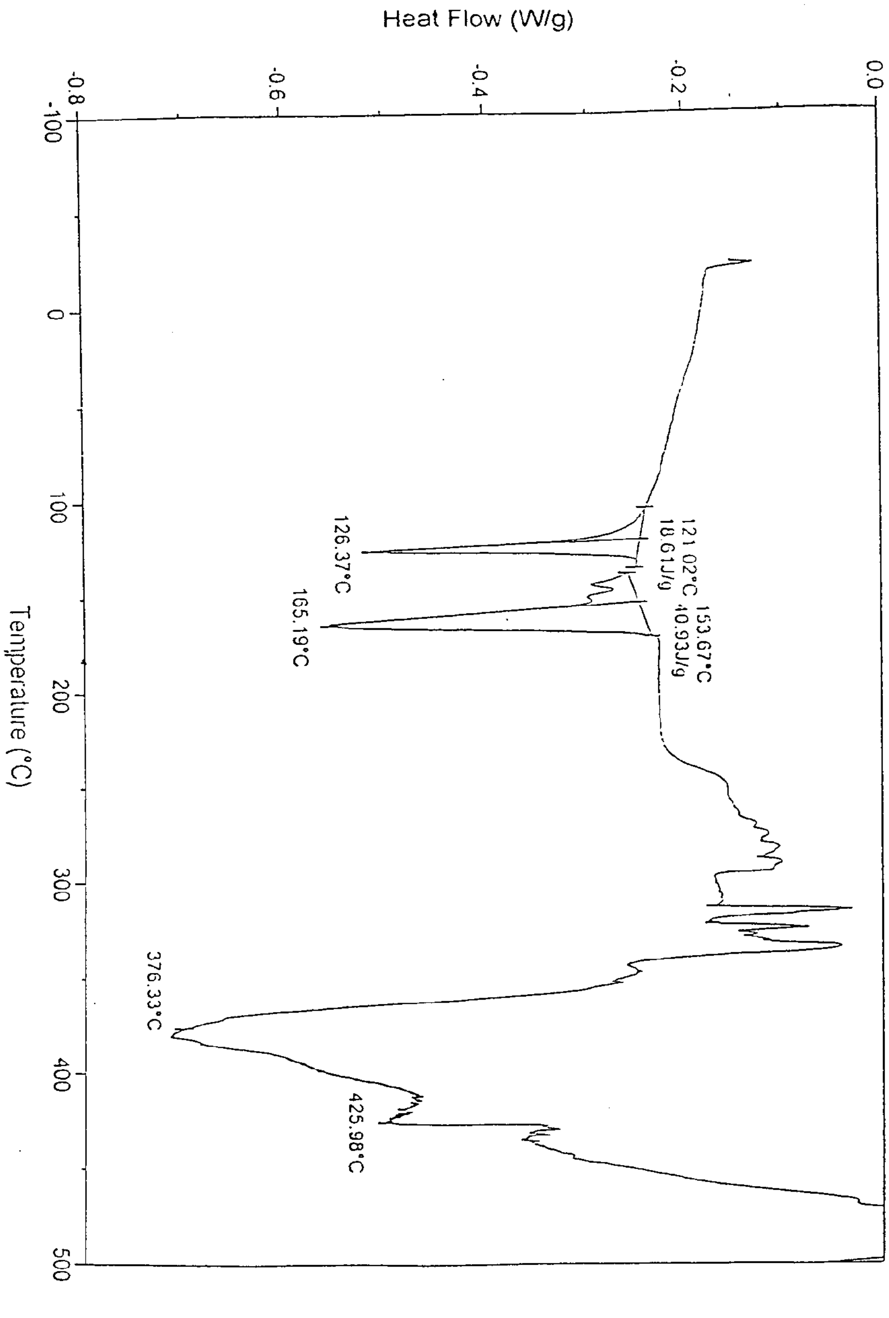
Heat Flow (W/g)
0.0
-0.2
-0.4
-0.6
-0.8
-100
0
100
200
300
400
500
Temperature (°C)
121.02°C
18.61J/g
126.37°C
153.67°C
40.93J/g
165.19°C
376.33°C
425.98°C

FIGURE 8

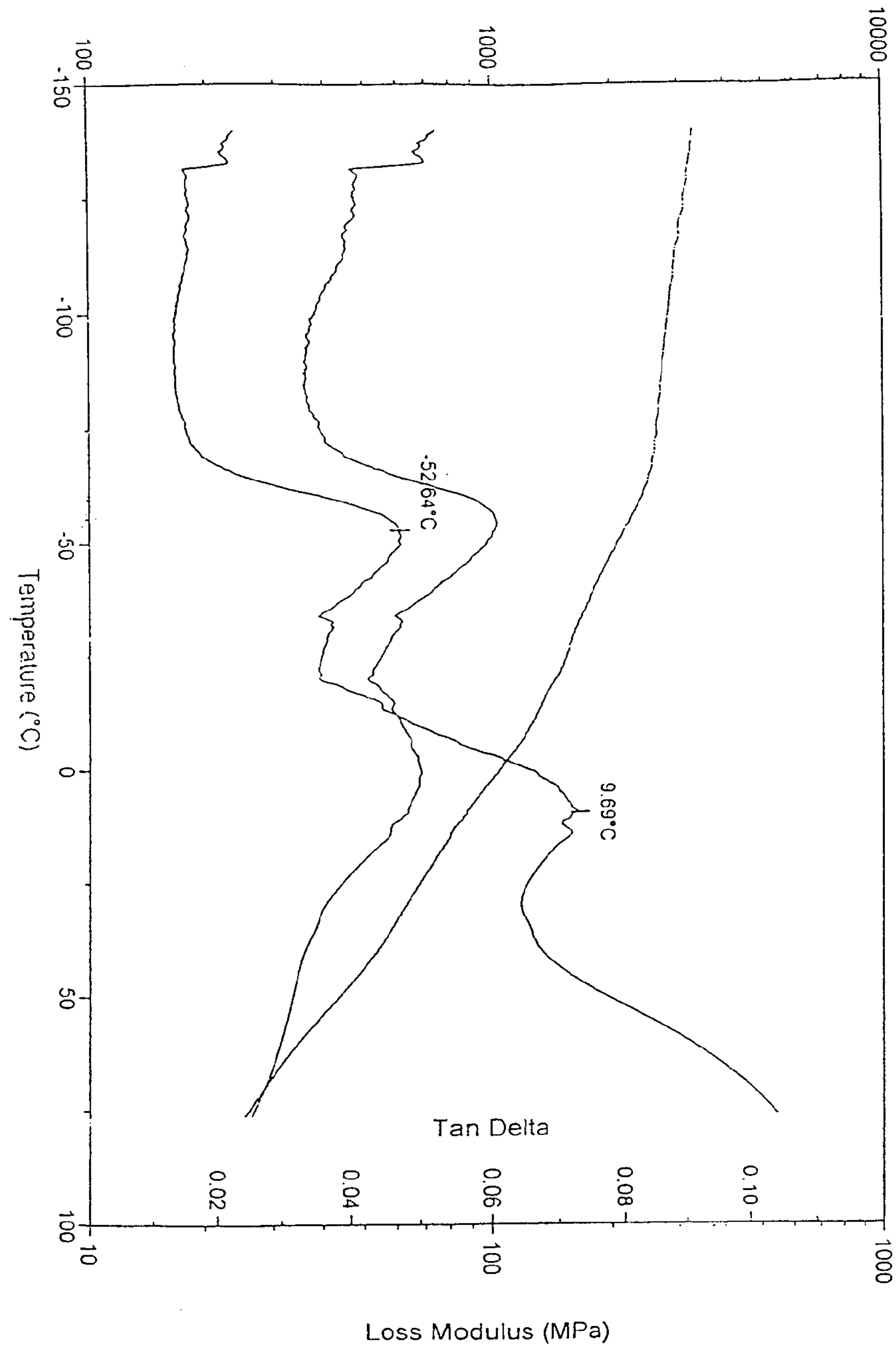

FIGURE 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 99/01074

A.	**CLASSIFICATION OF SUBJECT MATTER**
Int Cl^{7}:	C08L 7/00, 7/02, 9/02, 9/04, 77/06, 23/06, 23/08, 23/12, 75/04
According to International Patent Classification (IPC) or to both national classification and IPC	
B.	**FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
C08L 7/00, 7/02, 9/02, 9/04, 77/06, 23/06, 23/08, 23/12, 75/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT: WPAT, JPAT
NATURAL RUBBER; PVA; EVA; NITRILE BUTADIENE RUBBER; POLYESTER; POLYAMIDE; POLYETHYLENE.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 107197A (BECTON, DICKSON AND COMPANY), 2 May 1984 . See claims 1-23	1-68
X	GB 1473241A (DUNLOP LIMITED), 11 May 1977. See whole document	1-68
X	WO 9620738A (KIMBERLY_CLARK CORPORATION), 11 July 1996. See page 12, lines 8-24; claims 1-8 and 18	1-68

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 8 February 2000	Date of mailing of the international search report 11 FEB 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **DR. A. TESSEMA** Telephone No.: (02) 6283 2271

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 99/01074

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4634626A (YAMAGUCHI et al), 6 January 1987. See col. 2, line 39 - col.3, line 9; col.3, lines 51-66; claims	1-68
X	Derwent Abstract Accession No. 85-246459, Class P73, and JP 60-162628A (CHIR), 24 August 1985. See abstract	1-68
X	Derwent Abstract Accession No. 93-299329, Class P42 P73, and JP 5-212829A (SEKI), 24 March 1993. See abstract	1-68
X	Derwent Abstract Accession No. 90-018263, Class P73, and JP 1-297443A (JAPS), 30 November 1989. See abstract	1-68
X	Derwent Abstract Accession No. 88-216650, Class P73, and JP 63-152471A (IKED), 24 June 1988. See abstract	1-68
X	Derwent Abstract Accession No. 89-202015, Class A93, and JP 1-139634A (JAPAN SYNTHETIC RUBBER), 1 June 1989. See abstract	1-29

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 99/01074

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP	107197	CA	1221282	DK	4847/83	ES	526699
		ES	8504556	JP	59095135	JP	63243310
		US	4515851	US	4514460	US	4555813
		US	4589940	US	4567612	US	4569707
		CA	1224365	DK	3388/84	EP	134484
		ES	8505866	JP	60038146	MX	160361
GB	1473241	AU	77288/75				
WO	9620738	AU	46051/96	CA	2209154	EP	800409
		PL	321021	US	5641562		
US	4634626	GB	2172623	JP	61188138	NL	8600385

END OF ANNEX